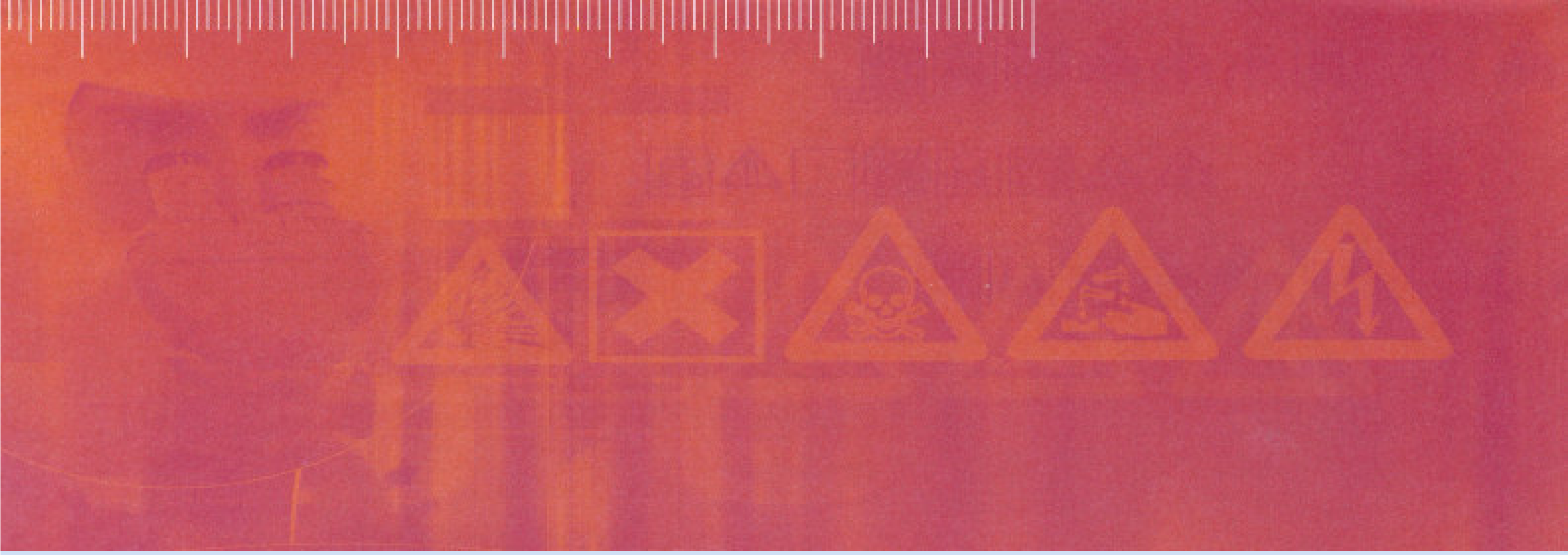

WORK STUDY 20/12/2005
N° 10072

AMMONIA

Large-scale atmospheric dispersion tests

INERIS

maîtriser le risque
pour un développement durable

AMMONIA

Large-scale atmospheric dispersion tests

INERIS – Accident Risks Division

Translation of the French report:

AMMONIAC : Essais de dispersion d'ammoniac à grande échelle – INERIS-DRA-RBo-1999-20410. R. BOUET

FOREWORD

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TABLE DES MATIÈRES

1. INTRODUCTION

Within the scope of its activities relating to accidental risk, INERIS particularly needs to determine safety perimeters around industrial facilities. Following a loss of confinement on a facility, the risks involved may be instantaneous, such as the explosion of flammable substances, or delayed, such as toxic substance releases. This research programme has concentrated more specifically on the progression of a toxic cloud formed after an accidental release of pressurised liquid ammonia in storage.

The atmospheric dispersion study on ammonia is of major interest for two reasons. Firstly, ammonia is a widely used substance with a large number of applications, due to its chemical or physical properties. Secondly, ammonia is a highly toxic, corrosive, flammable and explosive substance under certain conditions. Note that the loss of confinement of a 22 tonne tank of ammonia on 24 March 1992 in Dakar caused a large number of deaths (129 deaths and over 1100 injured subjects), some of which occurred several weeks after the accident due to the toxicity of ammonia.

This research programme was essentially financed by the French Ministry for Territorial Development and the Environment. Six European industrial firms also contributed: Norsk Hydro (Norway), Grande Paroisse (France), Veba Oel (Germany), SKW Piesteritz (Germany), CEA-CESTA (France) and Rhône-Poulenc (France). At INERIS, the programme was organised and coordinated in the Accident Risks Division (DRA). It was started in 1995 and completed in 1999.

The main aims of this programme were:

- to analyse the risks represented by facilities using quantities of ammonia of up to a few dozen tonnes ;
- to complete knowledge on the atmospheric dispersion of ammonia in open and obstructed environments ;
- and to compare the test results with atmospheric dispersion models.

To this end, a large-scale test programme was conducted using a pressurised liquid ammonia tank. The tests took place on the CEA-CESTA site over a period from December 1996 to April 1997. The purpose of this test campaign was to measure the ammonia concentrations leeward from the release in order to obtain a clearer idea on the dispersion of ammonia in the atmosphere in the case of realistic releases, particularly in open or semi-obstructed environments.

The best-known pressurised liquefied ammonia dispersion tests are the Tortoise Desert tests conducted by Goldwire et al. (1985) and the FLADIS tests conducted by RISØ (1993/1994). The flow rates used during the Tortoise Desert tests and the FLADIS tests were of the order of 100 kg/s and 0.5 kg/s, respectively. The INERIS tests were carried out with intermediary flow rates of the order of 2 to 4 kg/s.

The report is organised as follows. After a description of main properties of ammonia in chapter 2, a summary of atmospheric dispersion in general and ammonia dispersion in particular is given in chapter 3. Then, the large-scale tests conducted within the scope of this programme are described in chapter 4. Finally, a summary of the analysis of the release conditions measurements and the measurements recorded leeward from the releases is given in chapter 5 and 6, respectively.

2. PROPERTIES OF AMMONIA

2.1 PHYSICAL PROPERTIES

This section is particularly based on the Air Liquide (1980), ULMANN (1985) and SNIE (1991) documents

2.1.1 General points

Ammonia is identified as follows (see table 1):

name	ammonia
CAS number	7664-41-7
EEC number	007-001-00-5
RTMD hazard code	268
UN number	1005
chemical formula	NH_3
molar mass	17.03 g

table 1

At atmospheric pressure and 20℃, ammonia is a colourless gas with a pungent, irritant characteristic odour.

2.1.2 Thermodynamic data

The main thermodynamic data for ammonia is as follows:

- Melting point: -77.7℃ ;
- Boiling point: -33.4℃ to 1.013 bar abs ;
- Variable vapour tension as a function of temperature (see table 2):

Temperature (℃)	-77.71	-33.4	-18.7	0	4.7	20	25.7	30	50.1	78.9
Absolute pressure (bar)	0.06077	1.013	2	4.29	5	8.56	10	11.66	20	40

table 2: Vapour tension of ammonia as a function of temperature

- Critical temperature : 405.55 K ;
- Critical pressure : 114.80 bar ;
- Melting heat at 1.013 bar : 332.3 kJ.kg^{-1} ;
- Vaporisation heat at -15°C : 1210 kJ.kg^{-1} (289.5 kcal.kg^{-1}) ;
- Vaporisation heat at -33.4°C : 1370 kJ.kg^{-1} (328 kcal.kg^{-1}) ;
- Dynamic viscosity of liquid at -33.5°C : 10.225 mPa.s.

One litre of liquid releases 947 litres of gas (expanded at 15°C, at a pressure of 1 bar).

2.1.3 Solubility

The solubility of ammonia in water is high. Table 3 gives the solubility of ammonia as a function of temperature (WHO, 1986).

Temperature (°C)	**Solubility (g/l)**
0	895
20	529
40	316
60	168

table 3: Solubility of ammonia as a function of temperature

In addition, the dissolution of ammonia in water is highly exothermic: 2000 kJ per kilogram of ammonia dissolved in water (i.e. 478.5 kcal.kg^{-1}). As an indication, the dissolution of one kilogram of ammonia releases enough energy to evaporate almost one and a half kilograms.

2.1.4 Density

- Gas ⇨ 0.772 kg.m^{-3} at 0°C
  ⇨ 0.610 kg.m^{-3} at 20°C
  i.e. a density of 0.597 with reference to air.
- Liquid ⇨ variable as a function of temperature as indicated in table 4:

Temperature (°C)	-40	-33.4	-20	-10	0	10	15	20	30	50	100	132.4
Density of liquid ammonia	690	679	659	647	634	621	617	607	592	558	452	235

(kg.m^{-3})												

table 4: Density of ammonia as a function of temperature

2.2 EXPLOSIBILITY AND FLAMMABILITY

The information given below is essentially based on the study conducted by INERIS (Abiven, 1991) at the request of the French Ministry for the Environment.

2.2.1 Explosibility limits

In the literature, different values exist in relation to the Lower and Upper Explosibility Limits (LEL and UEL). The French Ministry for Territorial Development and the Environment's Industrial Environment Department data sheet referenced TOX 003-06-1998 gives the following values: LEL 16% and UEL 25%. These values are also given by INRS (1989) and SAX (1996). Other authors give slightly different values: LEL 15% and UEL 28% according to NFPA (1994) and Medart (1979), LEL 15.5% and UEL 27% according to Weiss (1985).

2.2.2 Self-ignition temperature

The self-ignition temperature of a mixture of gas or vapour is the minimum temperature from which the mixture is the site of a sufficiently rapid chemical reaction for a flame to appear spontaneously and propagate throughout the mixture. The self-ignition temperature of ammonia recorded in the literature is 650°C (Chaineaux, 1991).

2.2.3 Minimum ignition energy

The ignition of a flammable mixture requires the local introduction of a certain quantity of heat. The evaluation of this quantity of energy required to ignite the mixture is relatively difficult.

Buckley and Husa (1962) determined the minimum ignition energy of ammonia using a capacitive system. In this way, they obtained a minimum ignition energy of 680 millijoules for ammonia.

Kramer (1985) obtained a minimum energy of 14 millijoules for an ammonia-air mixture. This value, very different to that obtained by Buckley and Husa, demonstrates the difficulty quantifying the release energy of the experimental systems used.

However, in spite of this lower value for the minimum ignition energy determined by Kramer, an air-ammonia mixture has a higher minimum ignition energy (1 to 2 orders of magnitude) compared to most air-hydrocarbon mixtures.

2.2.4 Extinguishing agents

The extinguishing agents that must be used consist only of CO_2 or powders whenever there is a possibility of liquid ammonia being present. In fact, if water comes into contact with liquid ammonia, heat is transmitted to the latter, thus favouring its vaporisation.

2.3 REACTIONS WITH CONTAMINANTS

Ammonia is used in the manufacture of a large number of nitrous substances. However, hazardous reactions exist with some compounds or families of compounds.

The mixture of ammonia with a contaminant may lead to the formation of explosive substances.

In its documentary note records (note 1024-84-76), INRS (1976) mentions substances inducing hazardous chemical reactions with ammonia, such as nitric acid, oxygen, boron or oxidants

2.3.1 Halogens and inter-halogens

Halogens (fluorine, chlorine, bromine, iodine) react strongly with ammonia and its solutions. Explosive reactions may also occur with the following substances: acetaldehyde, hypochlorous acid, potassium ferrocyanides. Explosive compounds such as nitrogen trihalides are produced.

For example:

- with **chlorine**, Cl_2, mixtures are explosive if they are heated or if chlorine is in excess, due to nitrogen trichloride formation ;
- with **bromine pentafluoride,** BrF_5, explosions are likely.

2.3.2 Heavy metals

Ammonia is capable of reacting with some heavy metals (silver, gold, mercury, etc.), to produce materials liable to explode violently when they are dried:

- with **gold chloride (III)**, $AuCl_3$, under a wide variety of conditions, the presence of ammonia results in explosive or fulminant compounds which explode when heated ;
- with **silver oxides**, AgO, Ag_2O, explosive substances are formed ;
- with **mercury**, Hg, the reaction gives substances which are highly explosive and detonate easily. No instrument containing mercury should be used if it is liable to come into contact with ammonia (B.I.T., 1993).

2.3.3 Oxidants and peroxides

Ammonia reacts with a large number of oxides and peroxides: cold chlorine peroxide, hot iodic anhydride, perchlorates, which induce a violent reaction at around 250°C. The mixture of an oxidant compound and liquefied ammonia is liable to explode under the effect of a shock.

For example:

- with **hydrogen peroxide**, H_2O_2, ammonia dissolved in 99.6% of peroxide gives an unstable solution which explodes violently ;
- with **nitryl chloride**, $ClNO_2$, the interaction is very violent, even at -75°C ;
- with trioxygen difluoride, F2O3, the reaction is liable to cause inflammations and explosions, even at -183°C. With solid ammonia, it reacts to produce inflammations or explosions;
- with oxygen, O2, if they are placed in contact in a cooling device, an explosion is liable to occur. In addition, in the presence of ammonia, oxygen can accelerate or induce corrosion.

2.3.4 Acids

With some acids, violent reactions are observed, such as:

- with pure hypochlorous acid, HClO, ammonia, in gaseous form, explodes on contact and releases chlorine;
- with nitric acid, HNO3, an ammonia jet burns in a nitric acid atmosphere

2.3.5 Other aspects

Ammonia can also cause incandescent reactions, for example:

- with boron, B, heated in a dry ammonia atmosphere;
- with chromic anhydride, CrO3, ammonia gas breaks down dry trioxide with incandescence at normal temperatures.

Ammonia can also form self-igniting mixtures:

- with boron, B, heated in a dry ammonia atmosphere;
- with chromic anhydride, CrO3, ammonia gas breaks down dry trioxide with incandescence at normal temperatures.

Ammonia can also form self-igniting mixtures:

- with **nitric acid**, HNO_3, (see section 2.3.4.);

- with **chromyl dichloride**, CrO_2Cl_2, ammonia can be ignited with this substance.

2.3.6 Stability

At normal temperatures, ammonia gas is a stable compound; its dissociation into hydrogen and nitrogen only starts at around 450 - 500°C. In the presence of some metals such as iron, nickel, osmium, zinc, uranium, this decomposition starts from a temperature of 300°C and is almost complete at around 500 to 600°C.

2.4 TOXICITY

2.4.1 General

With respect to ammonia toxicity, different published values are available for the same given effect.

There are three fundamental reasons for this:

- the lack of human testing for high concentrations ;
- the disparity of the subjects making up a human sample, compared to a sample of selected laboratory animals for which the response varies very little from one animal to another ;
- and the difficulty extrapolating results obtained from animal testing to humans.

The toxicity of ammonia gas is associated with its very high solubility and the alkalinity of the resulting solutions, rendering it an aggressive agent for mucosa and lungs.

While reliable values on daphnids or rats are available, toxicity on humans is more difficult to determine. In particular, the influence of the concentration or exposure time is difficult to assess. With this respect, a study on "acute ammonia toxicity" was conducted by INERIS (Auburtin, 1999).

Exposure to an ammonia-charge atmosphere may induce various types of physical effects detailed below:

- Ocular effects: may be induced by the effect of vapours, but also by liquid projections. They are conveyed by tear production, conjunctivitis liable to be accompanied by more or less deep corneal effects ;
- Skin effects: in the form of contact dermitis ;

- Respiratory effects: the inhalation of ammonia vapours induces irritation of the upper respiratory tract with sneezing, dyspnoea and coughing, the most severe stage being acute pulmonary oedema (APO). APO is an accident which occurs following the inhalation of vesicant gases (Cl_2, NH_3, SO_2) by breaking down the walls of the pulmonary alveoli which are then inundated with blood plasma. Fortunately, the olfactory detection threshold of ammonia is well below the concentrations considered to be hazardous ;

- Digestive burns: the ingestion of ammonia is followed by very intense painful phenomena with gastric intolerance, a state of shock sometimes accompanied by erythema or purpura. The most dangerous complication is swelling of the glottis.

In direct contact with the skin, liquid ammonia freezes the tissues and causes burns. Ammonia solutions are strongly alkaline and as such highly irritating for the mucosa, skin and eyes.

Recurrent long-term exposure to ammonia induces a higher tolerance. Odours and irritants are perceived with more difficulty.

The olfactory perception thresholds are very variable according to the subject, ranging from a few ppm to several dozen ppm.

2.4.2 Acute toxicology

On this point, the results are based on observations made in the case of accidents and not rigorous experiments; however, the irritation threshold has been measured on groups of volunteers.

The median lethal concentration (LC50[1]) values, 50 %, are essentially used to evaluate the fatal risks for humans, as it is impossible to conduct such experiments on humans.

Data relating to toxicity for humans can only be used if it is associated with:

- a concentration ;
- an exposure time ;
- and a likelihood of effects occurring.

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[1] LC50: value calculated on the basis of the substance concentration assumed to cause the death of 50% of the test population for a specified exposure time.

INERIS report (Tissot, 2003) provides the following values:

Time	1 min	3 min	10 min	20 min	30 min	60 min
Lethal Effect Threshold[2] (mg/m^3)	17 710	10 290	5 740	4 083	3 337	2 380
Irreversible Effect Threshold[3] (mg/m^3)	1 050	700	606	428	350	248
Odour (mg/m^3)	3.62 – 36.2 (i.e. ≈ 5 – 50 ppm)					

Note: for ammonia, 1 ppm = 0.70 mg.m^{-3} and 1 mg.m^{-3} = 1.43 ppm

table 5: Ammonia toxicity values from INERIS data sheet (Tissot, 2003)

The detection of ammonia by human smell depends on the subject's sensitivity. This olfactory limit is generally from a concentration between 5 and 25 ppm.

This value is well below the threshold corresponding to irreversible damage which is in turn markedly lower than the threshold for lethal effects. It is important to note that this aspect is not verified for other gases, such as carbon monoxide, for example, which is odourless.

2.4.3 Toxicology at the workplace

The authorised concentration for ammonia in working atmospheres is limited and monitored according to regulations in most industrialised countries. The values currently permitted, which may vary between countries, are generally between 25 and 50 ppm. Higher values are defined for short-term exposure or in emergency situations. The values selected in France are given in table 6 below.

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[2] Lethal effect threshold: Maximum concentration of pollutant in air at a given exposure time below which, in most subjects, no risk of death is observed.
The term "most subjects" excludes "hypersensitive" subjects such as those suffering from respiratory failure.

[3] Irreversible effect threshold: Maximum concentration of pollutant in air at a given exposure time below which, in most subjects, no irreversible effect is observed.
An irreversible effect corresponds to the persistence over time of a lesional or functional effect directly following exposure in an accidental situation (single and short-term exposure) resulting in incapacitating effects.

Name	Definition	Value (ppm)	Observations
TLVC	Threshold Limit Value Ceiling at the workplace for 15 minutes	50	Labour Ministry Circular dated 19 July 1982 France
MLV	Mean Limit Value at the workplace for an 8-hour shift	25	Labour Ministry Circular dated 19 July 1982 France

Note: for ammonia, 1 ppm = 0.70 mg.m^{-3} and 1 mg.m^{-3} = 1.43 ppm

table 6: Limit values for workplaces in France

2.4.4 Summary of results on human toxicology

The two tables below show different effects observed according to the concentration and exposure time.

Main results of experimental studies on humans

Concentration (ppm)	Time (minutes)	Number of subjects	Effects	Ref.
Odour				
			Perception (sensitive subjects)	IPCS, 1986
			Perception	IPCS, 1986
	30	8	Nuisance	Verbeck, 1977
Unspecified irritation				
50	10	6	Moderate irritation	Mac Ewan, 1972
30-50	5	10	Nasal dryness	Report, 1973
Ocular irritation and tear production				
130	5	10	Ocular irritation (5 subjects/10)	Report, 1973
110-140	30	8	Nuisance	Verbeck, 1977
150-200	360	6	Tear production, transitory discomfort	Ferguson, 1977
150-200		7	Onset of ocular effects (not specified)	Wallace, 1978
400	< 1	7	Ocular irritation	Wallace, 1978
600	30 sec	7	Tear production	Wallace, 1978
700	few sec.	7	Tear production	Wallace, 1978
1000	immediate	7	Tear production, impaired vision	Wallace, 1978

Respiratory tract irritation and respiratory function disorders				
130	5	10	Throat irritation (8 subjects out of 10)	Report, 1973
150	8-11	16	Respiratory function signs (exercise)	Cole, 1977
110-140	30	8	Throat irritation: nuisance	Verbeck, 1977
500	30	7	Respiratory tract irritation	Silverman, 1949
			Functional signs	
700	few sec.	7	Still breathable	Wallace, 1978
1000	1-3	7	Breathing intolerable	Wallace, 1978
Tolerable / intolerable concentration				
140	30-75	8	Departure from exposure chamber	Verbeck, 1977
			Intolerable score for non-experts	
1500	instantaneous	7	Departure from exposure chamber	Wallace, 1978

table 7: Effects of ammonia on humans

Table 7 is taken from the INERIS study (Auburtin, 1999) on the acute toxicity of ammonia.

As an indication, the NIOSH (1987) proposes an IDLH value (Immediately Dangerous to Life or Health) of 500 ppm for ammonia. Note that this IDLH value corresponds to a maximum concentration in air up to which a subject exposed for not more than 30 minutes may escape without risking irreversible effects.

Concentration in mg.m^{-3}	Effects	Exposure time
3.5	Perceptible odour for some subjects.	
18	Perceptible odour for most subjects.	Mean occupational limit value in France and in a number of countries
35 - 70	Perceptible irritation for most subjects, in the eyes.	Tolerable for up to 2 hours for subjects not accustomed to exposure; accustomed subjects may tolerate higher concentrations over the same period
87 - 100	Irritation of the eyes, nasal tract and mucosa. Irritation of the throat and respiratory tract.	Exposure time of over 1 hour.
140	Nausea and headaches.	
280 - 490	Immediate irritation of the eyes, nose, throat and upper respiratory tract.	Exposure for ½ hr to 1 hr does not cause serious damage although irritation of the upper respiratory tract may persist for 24 hrs following a 30-min exposure period. Aggravation of pre-existing respiratory problems may occur.
700 - 1400	Severe coughing. Severe irritation of the eyes, nose and throat, bronchitic spasms.	Damage to the eyes and respiratory system may occur if they are not treated quickly. A 30-min exposure period may induce very serious effects on subjects with a predisposition for respiratory problems.
2100 - 2800	Severe coughing. Severe irritation of the eyes, nose and throat.	May be fatal after 30 min.
3500 - 8400	Respiratory spasm. Rapid asphyxia, severe oedema, strangulation.	Fatal in a few minutes.

table 8: Effects on ammonia on humans according to concentration (EFMA-IFA, 1990)

Table 8 is taken from the "guide on risks represented by ammonia" issued by SNIE (1991).

2.4.5 Toxicology of fauna and flora

2.4.5.1 Animals

Table 9 shows some effects observed on animals

Species	Concentration in mg.m^{-3}	Effects
Pigs	75 - 100	Coughing, nasal, oral and lachrymal secretions.
	140	Severe symptoms of irritation and convulsion after 36 hrs of exposure with recovery 7 hrs after end of exposure.
Rabbits	280	A 10-min exposure period induces an irreversible cessation of ciliary activity.
	350	Same effects as above for a 5-min exposure period.
	3500	LC 50 – 1 hr.
Cats	3500	LC 50 – 1 hr.

table 9: Toxicological effects of ammonia on some animals according to concentration (EFMA-IFA, 1990)

2.4.5.2 Aquatic life

Free (non-ionised) ammonia in surface water is toxic for fish. However, ammonium ions are not. In this way, in the event of water contamination by ammonia, ammonia salts representing no toxic risk may be formed. The pH value of the water is important as free ammonia is formed for pH values greater than 7.5-8.0.

For trout, disorders occur from 0.3 mg.l^{-1}. Percidae (or castotomidae) and salmonidae are the most sensitive varieties for freshwater species. For seawater, prawns appear to be the most sensitive invertebrate species, Depending on the type of fish, a risk of mortality arises between 1.2 and 5 mg.l^{-1} (these values refer to non-ionised ammonia).

For ionised ammonia (ammonia in solution), lethal concentrations (LC50) for some species are given in the table below:

Species	Threshold	Exposure time	Concentration
daphnids	LC50	24 hrs	27 mg.l^{-1}
fish	LC50	24 hrs	182 mg.l^{-1}

algae	LC50	5 days	185 mg.l^{-1}

table 10: lethal concentrations (LC50) for some species

2.4.5.3 Plant life

Ammonia is considered as biodegradable and not accumulable, However, it requires monitoring in the form of an annual evaluation of water, air and soil releases for annual uses of over 10 tonnes.

Ammonia can be toxic for some plants as it cannot be excreted. It is assimilated by combining with carbonate chains, and, in this way, the excess ammonia can pass into the sugar metabolism.

Other plants have functions enabling the assimilation of ammonia thus allowing them to tolerate ammonia or use it preferentially.

3. ATMOSPHERIC DISPERSION

3.1 CONTEXT

Knowledge of the atmospheric dispersion mechanisms of ammonia is applied in the following three cases:

- The predictive nature of an atmospheric dispersion study makes it possible to envisage the potential risks of an industrial facility, particularly within the scope of hazard studies or impact studies ;
- In the event of an accidental situation, modelling the atmospheric dispersion makes it possible to evaluate the measures to be taken in real time ;
- Following an accident, the analysis of the dispersion conditions in the atmosphere can give a clearer understanding of the causes of these accidents, and in some cases, validate atmospheric dispersion models used for the above mentioned studies.

There are different approaches to the study of atmospheric dispersion:

- full-scale tests ;
- model (hydraulic or aeraulic) simulation ;
- use of mathematical calculation codes.

The last way to approach gas transportation and diffusion phenomena in the atmosphere offers advantages over the techniques mentioned above such as the fact that complex experimental procedures are not used, the rapid nature of the study, and the possibility of envisaging a large number of cases.

However, in order to be able to access simulation, it is necessary to have extensive knowledge of the phenomena governing atmospheric dispersion. With this respect, full-scale tests are required.

Studying the atmospheric dispersion of ammonia is of major interest for two reasons. Firstly, ammonia is a very toxic, corrosive, flammable and explosive substance under certain conditions. Secondly, ammonia is a very widely used substance with numerous applications, due to its chemical or physical properties.

With respect to its chemical properties, the main application of ammonia is the manufacture of fertilisers. Ammonia represents the main concentrated source of nitrogen for agriculture, which consume approximately 85 to 90% of production. Industry uses ammonia as a raw material for the manufacture of explosives, fibres and plastics. It is also used in the manufacture of paper, rubber, in refineries, the leather industry and the pharmaceutical industry.

With respect to applications associated with physical properties, ammonia is used as a coolant in compression and absorption systems. Some characteristics of ammonia, such as its high latent heat, its low vapour density and its chemical stability, favour its use in major industrial facilities.

These two specificities of ammonia, its harmfulness and its widespread use require, in terms of personal safety, details on its behaviour in the event of loss of confinement, particularly in the case of accidental releases into the atmosphere.

Therefore, to this end, this chapter proposes to:

- provide a status report on atmospheric dispersion tests conducted with ammonia ;
- present the state of the art and gaps in the knowledge of the modelling of the atmospheric dispersion of ammonia, as the modelling of the atmospheric dispersion represents a key stage in the study of toxic substance release ;
- and justify the study areas developed within the scope of this research programme.

3.2 ATMOSPHERIC DISPERSION TESTS

After a description of the main characteristics of ammonia releases, this section first presents atmospheric ammonia dispersion tests and then briefly presents dispersion tests conducted with heavy gases.

3.2.1 Characteristics of accident ammonia releases

The atmospheric dispersion of a gas is influenced by the release conditions, the weather conditions and also by the type of gas released.

There are different possible types of accidental ammonia releases:

- ammonia gas jet from a pressurised vessel (release from gaseous phase) ;
- two-phase ammonia jet from a pressurised vessel (release from liquid phase) ;
- evaporation of a pool of liquid ammonia in which the temperature is less than or equal to its boiling point[4] ;
- leakage of liquid ammonia from a cryogenic tank (liquid ammonia at a temperature below the boiling point and at atmospheric pressure).

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[4] Note that the boiling point of ammonia at normal pressure is -33.4℃.

Ammonia has specific dispersion characteristics and depending on the type of release, the dispersion of the ammonia released will be different. The type of release, which was more specifically studied within the scope of this programme, is the two-phase ammonia release from the liquid phase of a pressurised tank.

All the studies conducted on two-phase releases break down the jet into three main zones as shown in *figure 1* below:

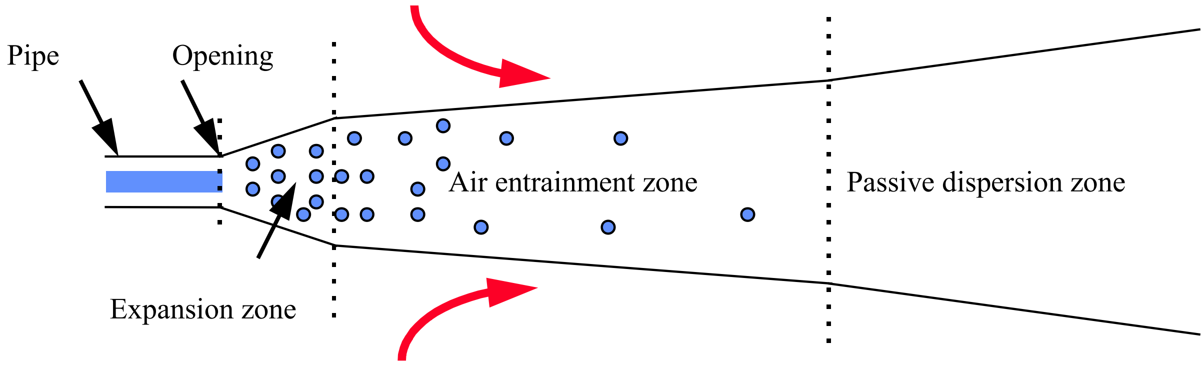


figure 1: two-phase jet

These three main zones are respectively:

- ***the expansion zone***: In this short zone, between 0.5 and 4 times the diameter of the opening (IANELLO, 1989), the fluid is expanded from the pressure at the opening to atmospheric pressure. Due to this sudden depressurisation, the liquid phase of the release is in a superheated state and a fraction of this liquid phase is vaporised almost instantaneously. This phenomenon is known as the "*thermodynamic flash*". The gaseous phase created by this flash phenomenon will have, due to its lower density, a higher velocity than that of the liquid. This difference in velocity between the two phases induces the entrainment of the liquid phase and its fragmentation into fine droplets. These droplets are entrained by the gaseous phase at a high velocity and form what is referred to as the "*aerosol*".
  In this way, at the end of this zone, the jet consists of a gaseous phase and a liquid phase in aerosol form and it is commonly admitted that the entire jet (liquid and gaseous phases) is at the boiling point of the released substance.

- ***the entrainment zone***: In this zone, the turbulent jet induces the entrainment of the ambient air in the jet. The energy supplied by this air which is warmer than the jet is initially used to vaporise the liquid droplets present in the jet. This vaporisation cools the jet which then behaves like a jet of heavy gas in the atmosphere.
  Once the liquid phase has been entirely vaporised, this energy is used to heat the jet which has become entirely gaseous.

- ***the passive dispersion zone***: With the entrainment of air, the velocity of the jet progressively decreases until it reaches the wind velocity. From this point, the jet is said to be dispersed passively in the atmosphere.

The presence of obstacles is also a factor in the atmospheric dispersion of heavy gases, particularly liquefied ammonia.

If the obstacle is sufficiently close to the release, it will modify the initial dispersion phase and subsequently, it will influence the dispersion in the atmosphere. For example, a two-phase release in jet form, which encounters an obstacle such as a wall or floor, may result in pool formation. In this case, the dispersion of the ammonia from the pool is different to that which would have followed the free jet.

On the other hand, if the obstacle is at a distance from the release point, and if the size of the cloud formed by the ammonia is comparable to the obstacle, the obstacle only modifies the gaseous mass flow and will not modify the physical state of the release. In this case, the effect on dispersion will be less than in the previous case, decreasing according to the dilution and size of the cloud when it encounters the obstacle.

3.2.2 Tests by A. Resplandy

The information contained in this section is based on the A. Resplandy's summaries (1967, 1968, 1969).

3.2.2.1 Context

In order to determine the measures to be recommended for the safety of the vicinity of liquefied ammonia storage tanks, A. Resplandy, Official Inspector of Classified Facilities and Chairman of the Consultative Committee for Classified Facilities, conducted two series of liquid ammonia dispersion experiments. They took place, firstly at the Boissise-la-Bertrand army camp in June 1967 and, secondly, at the Mourmelon army camp in March 1968.

The purpose of the experiments was to:

- specify the conditions under which ammonia is diffused into the atmosphere from a liquid phase spillage in order to determine the radius of the isolation zones to be stipulated around pressurised storage tanks ;

- examine the extent to which refilling of liquid ammonia can be envisaged ;

- test the effectiveness of the intervention resources provided to Civil Protection teams called upon to intervene in the event of an accidental liquid ammonia leakage.

3.2.2.2 Test conditions

A – Tests at Boissise-la-Bertrand, June 1967

The liquid ammonia tanks consisted of:

- a semi-trailer tanker containing 15 tonnes of ammonia at a pressure of 7 bar, equipped with a 2 inch pipe with a flow rate of approximately 20,000 kg/hr (5.5 kg/s) in liquid phase and a 1 inch conduit with a flow rate of 100 kg of liquid ammonia in approximately 70 seconds (1.4 kg/s) ;
- a tractor-drawn replenishment vehicle comprising two ammonia tanks at 7 bar with a unit capacity equal to 2000 kg, each tank being equipped to release in liquid phase via a 1¼ inch pipe or in gaseous phase via a ¾ inch pipe.

The tests were conducted on 28 June 1967 between 6 am and 11 am. The ground temperature rose gradually from 13°C to 17°C. The relative humidity was maintained in the vicinity of 85%. The wind velocity varied from 0 to 3 m/s.

Two types of measuring device were used:

- 17 Dräger manual detectors:

  The Dräger units essentially consisted of a bellows pump used to pass a given volume of gas through a calibrated tube filled with coloured reagent. Three types of calibrated tubes were used:

  - 0.5/a type: sensitivity from 5 to 70 ppm (non-interpretable measurements) ;
  - 25/a type: sensitivity from 50 to 700 ppm ;
  - 0.5%/a type: sensitivity from 0.5 to 10% (non-interpretable measurements).

  Note that these measuring devices only gave mean values calculated over variable periods (since the number of pump strokes is not constant according to Resplandy) and only allowed a single measurement per test.

- Hartmann and Braun Caldos 2 continuous thermal conductibility analyser:

  This unit equipped with a 4-6 mm diameter and 60 m long probe-conduit was operated coupled with a Philips potentiometric recorder over the following three sensitivity ranges: 0 to 2%, 0 to 4%, 0 to 10%.

Three types of releases were used in order to study:

- the atmospheric diffusion of ammonia from a liquid phase leakage:

  - *without curtain interposition*, using a 2 inch conduit ending with a 90° bend to release vertically upwards, and producing approximately 9 releases per minutes, i.e. a released quantity of approximately 330 kg of liquid ammonia ;
  - *with curtain interposition,* using a 1 inch conduit ending with a 90° bend fitted to a cylindrical vessel in order to be able to guide the jet upwards, as above, or towards the base of the vessel, located 15 cm from the end of the conduit, and performing 2 tests of approximately one minute (one with an upward jet, the other with a downward jet) ;
- retrievable liquid ammonia refilling possibilities after a storage tank accident,
- intervention resources in the event of a liquid phase (aerosol) ammonia leakage via the effect of water and heat.

B – Tests at Mourmelon, March 1968

The ammonia was supplied by a 15000 kg semi-trailer tank identical to that for the previous tests, able to release in liquid phase via a 50 mm diameter pipe, and in gaseous phase via a 30 mm diameter pipe.

The tests were conducted on 28 March 1968 between 8 am and 12:30 pm. The ground temperature rose gradually from 8℃ to 18℃. The relative humidity varied from 95% to 80%. The wind velocity was between 0 and 3 m/s.

Three recording analysers were used:

- *Hartmann and Braun Caldos 2* continuous thermal conductibility analyser identical to that used above ;
- Kuhlmann conductimetric analyser equipped with a 50 m probe operating over the 0 to 0.5% range ;
- "ONERA SO" type IR spectrometry analyser equipped with a 50 m probe operating over the 0 to 0.1% range.

Three types of releases were studied:

- the atmospheric diffusion of ammonia from a liquid phase leakage:
  - in the case of a release into a stable atmosphere with a vertical ejection ;
  - by varying the orientation of the ejection conduit ;
  - by monitoring the progression of the aerosol in terms of stabilised flow rate ;
  - by observing the contamination of the atmosphere of a residential building (caravan) flushed with the ammonia cloud.
- gaseous phase leakage simulation in a pressurised storage tank:

  - by varying the direction of ejection ;
  - by inserting a curtain during vertical ejection.
- handling of liquid ammonia in the open air:
  - by studying the effectiveness of the clay and cement retention dikes ;
  - by observing the effect of water on liquid ammonia.

3.2.2.3 Results

In these publications, A. Resplandy (1967, 1968, 1969) gives the following main results.

Liquid phase leakages induce the formation of an aerosol, which, before dissipating, may travel several hundred metres at ground level propelled by the wind. In fact, ammonia's particularly high latent heat of vaporisation only allows very slow evaporation of the micro-drops.

The ammonia aerosol is carried by the wind, even if the wind velocity is extremely low, covering a relatively narrow area, without any diffusion upstream from the release point. Propagating against the ground, the ammonia droplets may be deviated from the trajectory given to them by the wind by large obstacles.

An ammonia aerosol is dissipated completely a few minutes after the release causing it has stopped and there is no residual hazardous concentration for humans on the zone covered.

For the same mass of liquid ammonia ejected into the atmosphere from a pressurised storage tank, aerosol formation decreases as the temperature of the liquid approaches its boiling point at atmospheric pressure.

In the open air, it is not possible to block the progression of ammonia droplets effectively with a water spray, even if it is considerable in size.

The relatively rapid diffusion of gaseous ammonia in the atmosphere makes it possible to envisage, if required, stabilisation by decompressing the contents of non-cooled tanks, followed by handling of the stabilised liquid ammonia in the open air.

Finally, it was demonstrated how dangerous it could be to intervene with water on a sheet of liquid ammonia. In fact, this action results in a significant release of gas and aerosol.

In a liquid phase release from a pressurised ammonia storage tank, by adjusting the ejection mode (inserting a curtain, direction control), there are limited options available to reduce aerosol formation and decrease the distance covered by the aerosol front.

Pollution at ground level can be limited by discharging gaseous ammonia vertically into the atmosphere from a pressurised tank.

A well-designed system makes it possible to equilibrate the liquid from a pressurised tank in the open air by eliminating the vapour phase in the atmosphere.

Liquid phase ammonia equilibrated at atmospheric pressure can be effectively collected and stored in the open air in a retention dike; however, the temperature rise on the casing walls is accompanied by gas and aerosol emission.

The atmospheric dispersion tests conducted by A. Resplandy were among the first. They resulted in qualitative observations rather than genuinely interpretable quantitative data. In fact, not many parameters were measured and recorded. In particular, there was no precise characterisation of the atmosphere, or precise measurements of the ammonia concentration leeward from the release.

These tests particularly made it possible to give ideas on the behaviour of ammonia in the event of an accidental release and outline the perspectives to be studied. In this way, A. Resplandy proposes three areas of study to complete the study conducted:

- specify the influence of the leakage flow rate on the characteristics of the aerosol formed ;
- observe the influence of weather conditions on aerosol characteristics in more detail ;
- determine the optimal conditions to return pressurised tanks to atmospheric pressure.

3.2.3 Tortoise Desert tests

The releases produced for the Tortoise Desert tests (Goldwire, 1996) were very different to those used by Resplandy.

For example, the quantity of ammonia released on average during the tests conducted by Resplandy in 1967 and 1968 was of the order of 300 to 500 kg with a maximum of 1000 kg for times between 1 and 6 minutes, while for the Tortoise Desert tests, the quantities released were between 10,000 and 41,000 kg.

3.2.3.1 Context

A series of 4 ammonia dispersion tests was conducted during the summer of 1983 by the Lawrence Livermore National Laboratory in the United States. These tests are frequently referred to as the Tortoise Desert Tests in the literature. They were used to study the dispersion of pressurised liquid ammonia releases in the atmosphere.

3.2.3.2 Test conditions

Two tankers with a capacity of 41.5 m^3 were used for the tests. Nitrogen tube trailers were connected to the two tankers in order to maintain the pressure inside the tankers.

The first test was conducted with a 3.19 inch (81 mm) release orifice and the three others were conducted with a 3.72 inch (94.5 mm) diameter orifice. The release was horizontal, in the direction of the wind and at a height of 0.79 metres above ground level.

Table 11 below shows the main characteristics of these releases:

Test	Date	Release volume in m^3	Release mass in kg	Release time in s	Flow rate in kg/s	Wind velocity in m/s	Wind direction	Stability class
1	24/08/83	14.9	10,200	126	81	7.4	224°	D
2	29/08/83	43.8	29,900	255	117	5.7	226°	D
3	01/09/83	32.4	22,100	166	133	7.4	219°	D
4	06/09/83	60.3	41,100	381	109	4.5	220°	E

table 11: Characteristics of releases produced during Tortoise Desert tests

Two main devices were used to measure the meteorological data and the concentrations for the dispersion study.

With respect to the dispersion study, the vapour concentrations were measured by:

- 20 MSA NDIR gas sensors positioned 100 m from the source and such that the gas plus the aerosol passed through a heating device intended to vaporise the aerosol so as to determine the total quantity of NH_3 ;
- 31 LLNL IR gas sensors positioned 100 m and 800 m from the source and initially devised for liquid natural gas (LNG) dispersion tests and not optimised for ammonia detection, but they made it possible to detect concentrations above 1% ;
- 24 IST sensors located 0, 800, 1450, 2800 and/or 5500 m from the source.

The data acquisition and storage system used UHF radio waves for data transmission. All the data acquisition stations and all the stations were portable, battery-operated and gas-tight.

3.2.3.3 Results

The first two tests were conducted on a water-saturated site due to heavy rain. The site was almost completely dry for the third test and completely dry for the fourth, such that the overall weather conditions were more variable than planned.

Test No. 4, the most significant in terms of released quantity, was conducted under the most stable atmospheric conditions. It demonstrated that the jet was visible up to a distance greater than 100 m from the source. The dimensions of this cloud, which was heavier than air, are approximately 70 m wide and less than 6 m high. The maximum gas concentration observed at 100 m was 6.5% according to Goldwire (1986) and 10% according to Koopman et al (1986). The cloud had spread over a width of 400 m when it reached 800 m, its height was still 6 m. The heavy gas and jet effects dominated the dispersion.

Table 12 below defines some orders of magnitude based on experimental results. It shows maximum concentrations recorded according to the leeward distance from the release site.

Distance	**100 m**	**800 m**	**1450 m**	**2800 m**	**5500 m**
Maximum concentration recorded	6 to 10%	1.4 to 1.6%	> 0.5%	> 0.5%	100 to 200 ppm

table 12: Maximum concentrations observed as a function of leeward distance from the release site according to Koopman et al. (1986) and Goldwire (1985, 1986).

Goldwire et al. (1986) demonstrated the need for "enhanced" simple models to predict the effects of accidental releases. In addition, Hanna et al. (1993) also use Goldwire's results (1985) to compare the results of the models and the experimental results. The table below gives the concentrations observed on the plume axis.

Tortoise Desert tests	**1**	**2**	**3**	**4**
Flow rate (kg/s)	81	117	133	109
Concentration at 100 m (ppm)	49,943	83,203	76,881	57,300
Concentration at 800 m (ppm)	8,843	10,804	7,087	16,678

table 13: Concentrations observed on plume axis during Tortoise Desert tests according to Hanna et al. (1993).

These results should be compared to the information contained in table 12.

In relation to these results, several remarks should be noted:

- The highest concentration at 100 m is obtained for test 2 despite a higher flow rate for test 3. The wind velocity for test 2 was lower (5.7 m/s) than for test 3 (7.4 m/s) and the outdoor temperature was 3°C lower for test 2 compared to test 3 ;
- At 800 m, the highest concentration is obtained for test 4, with the lowest flow rate among the releases produced with the 3.72 inch orifice (tests 2, 3, 4). On the other hand, the concentration at 100 m was the lowest. This result is explained by most stable weather conditions, stability class E instead of class D for tests 2 and 3 ;
- Among all the tests, the most unstable weather conditions were recorded during test 3 (Goldwire, 1985). Under these conditions, in spite of a higher release flow rate, the concentration observed on the plume axis at 800 m proves to be the lowest.

These remarks demonstrate that the weather conditions are a very important factor in atmospheric dispersion at longer distances, i.e. beyond 100 metres. It is not sufficient to characterise the source term in detail to model the atmospheric dispersion of ammonia, the weather conditions are also required.

Note: The 4 sections below (§ 3.2.4 to 3.2.7) are essentially based on the document produced by Wheatley (April 1987).

3.2.4 Unie van Kunstmest Fabrieken bv tests, Netherlands, 1972

The Unie van Kunstmest Fabrieken bv tests, Netherlands, 1972 were conducted by J. W. Frenken and were reported by Blanken (1980).

The test conditions were as follows:

- vessel containing ammonia at 3.5 bar / 0°C ;
- 8 mm diameter release nozzle ;
- ambient temperature of -10°C ;
- and wind velocity of the order of 2 to 3 m/s.

The purpose of these tests was to measure the quantity of ammonia collected on the ground in the case of two one-minute releases each releasing 38.4 kg (0.64 kg/s) in the following configurations:

- a horizontal release perpendicular to the wind, located 1800 mm from ground level. This release made it possible to collect 5.5 kg of liquid ammonia on the ground, i.e. 14.3% of the ammonia released ;

- a vertical release directed towards the ground, 2000 mm from ground level, making it possible to collect 27.3 kg of liquid ammonia on the ground, i.e. 71.1% of the ammonia released.

The measurement method for the quantity of ammonia collected is not specified. No measurements of the concentration in the air were made

3.2.5 Imperial Chemical Industries tests, United Kingdom, 1974

The Imperial Chemical Industries tests, United Kingdom, 1974, were reported by Reed (1974).

The purpose of the tests was the characterisation of the effectiveness of pressurised storage tank retention dikes.

Two series of tests were conducted:

- one series intended to simulate the disaster-related rupture of a container by suddenly removing a lid. The results of these tests are not described by Wheatley (April 1987);
- another series of releases via a 1 mm diameter orifice linked by a tube to a tank containing ammonia at 6.5 bar/16°C, located 1 m from ground level at various angles. When the orifice was horizontal or pointing slightly upwards, an aerosol cloud was formed and no liquid formation was observed on the ground. When it was pointing slightly downwards, a small fraction of liquid ammonia was collected. The quantity is not specified in Wheatley's report (April 1987).

No other observations were made, and no air concentration measurements were made.

3.2.6 Unie van Kunstmest Fabrieken bv tests, Netherlands, 1980

The Unie van Kunstmest Fabrieken bv tests, Netherlands, 1980, reported by Blanken (1980), used ammonia stored at 13.4 bar at 38°C and released via a 100 mm long and 2 mm diameter capillary tube into moist air.

The purpose of the tests was to study the size of the droplets in the jet. Only qualitative results were obtained.

In an ammonia atmosphere, the jet was transparent and the liquid separated from the jet and formed a pool on the ground.

In the moist air, the jet was opaque and the liquid ammonia was not collected. It was assumed that the ammonia aerosol initially formed was rapidly vaporised when it was diluted with air. In addition, it was concluded that the opacity was caused by water condensation, which forms an aqueous ammonia aerosol.

No concentration measurements were made.

3.2.7 .Landskrona tests, Sweden, 1982

The Landskrona tests, Sweden, 1982 were conducted by the Swedish National Defence Research Institute and were reported by Nyrén et al (1983).

The test conditions were as follows:

- a commercial vessel containing 1400 kg of ammonia at 6 bar and 9°C ;
- an ambient temperature of 8°C and 42% relative humidity ;
- and a wind velocity of 13 m/s.

The purpose of these tests was to measure the flow rate of a two-phase ammonia release and compare it to a theoretical model.

The releases were produced from a tube with an internal diameter varying between 32 and 40 mm. Six tests were conducted with a 2 m long tube and five with a 3.5 m tube. In each case, the tube was located 2 m above ground level. Each release lasted 60 to 90 s.

For all the tests, except for four, the tank pressure varied considerably. For the remaining four, the outlet pressure was 2.2 bar and the mass flow rate 2.2 kg/s. The jet touched the ground at a point located between 6 and 10 m from the release point. No pool was observed.

No concentration measurements were made.

3.2.8 FLADIS programme tests

Ammonia releases were produced within the scope of a European test programme called FLADIS (Research on the dispersion of two-phase flashing releases). This programme was conducted under the aegis of DG XII in Brussels (Nielsen & Ott, 1996).

Three measurement campaigns were conducted in April and August 1993 and in August 1994. In total, 27 horizontal releases of pressurised liquefied ammonia were produced.

The release flow rates varied from 0.25 to 0.55 kg/s via 4.0 and 6.3 mm diameter orifices. The longest test lasted 40 min.

One of the aims of the FLADIS programme was to study in detail the aerosol jet in the near field, the heavy gas dispersion phase and the transition from passive dispersion. For this, sensors were positioned in an arc shape centred on the release point at 20 m, 70 m and 240 m.

Aerosol composition measurements in the two-phase jet were made during the tests. On the basis of these measurements, it was observed that the aerosol, which consisted of almost pure ammonia close to the release point, consisted, within a few meters, of almost pure water.

In addition, no rise in the ammonia cloud was ever observed during the releases.

3.2.9 Tests conducted at Ecole des Mines, Alès

Ecole de Mines, Alès, has conducted several ammonia dispersion test campaigns since 1996. The tests are conducted using one or two 44 kg ammonia cylinders placed upside down so as to produce liquid phase releases (Bara, Dussere, 1996). The purpose of these tests is to study the effectiveness of the peacock tail hoses used by the fire services.

Downstream from the peacock tail hoses located approximately 1 metre from the cylinders, a reduction in the ammonia concentrations was observed on the release axis, by a factor greater than 10 at a 13 m distance from the cylinders and a factor of at least 3 at a 20 metre distance. On the other hand, no significant reduction was observed beyond 50 metres.

3.2.10 Other atmospheric dispersion tests

Within the scope of this programme, substance dispersion tests in the atmosphere with gases other than ammonia were taken into consideration.

As mentioned above, ammonia released into the atmosphere generally results in the formation of a cold cloud, heavier than air. Therefore, dispersion is carried out as for that of a heavy gas until a sufficient level of dilution is reached so that the ammonia dispersion is governed solely by the characteristics of the atmospheric flow (passive dispersion).

For this reason, atmospheric dispersion tests conducted on heavy gases are of interest for the study of the atmospheric dispersion of ammonia. This is particularly true for all aspects relating to the initial release phase.

Table 14 overleaf summarises the main dispersion tests relating to heavy gases.

Note: The Tortoise Desert tests are included in this table for comparison purposes

	Burro	**Coyote**	**Tortoise Desert**	**Goldfish**	**Handford**	**Maplin Sands**	**Prairie Grass**	**Thorney Island (instantaneous)**	**Thorney Island (continuous)**
Substance	LNG	LNG	Ammonia	Hydrogen fluoride	Krypton 85	LNG and LPG	Sulphur dioxide	Freon and nitrogen	Freon and nitrogen
Release type	Boiling liquid	Boiling liquid	Two-phase releases	Two-phase releases	Gaseous	Boiling liquid	Gaseous jet	Gaseous	Gaseous
Number of tests	8	3	4	3	5	4 and 8	44	9	2
Quantities in kg	10700 to 17300	6500 to 12700	10000 to 36800	3500 to 3800	11 to 24 Curies	LNG: 2000 to 6600 LPG: 1000 to 3800	23 to 63	3150 to 8700	4800
Time in s	79 to 190	65 to 98	126 to 381	125 to 360	598 to 1191	60 to 360	600	instantaneous	460
Surface type	Release on small stretches of water	Release on small stretches of water	Moist sand	Dry lake bed	Desert with bushes	Release on shallow stretches of water	Grass	Grass	Grass
Stability classes	C-E	C-D	D-E	D	C-E	D	A-F	D-F	E-F
Maximum observation distance	140 - 800	300 - 400	800	3000	800	400 – 650	800	500 - 580	472

table 14: Summary table of main dispersion tests relating to heavy gases

Note: Thorney Island, 19 tests during phase I; 9 tests during phase II and 3 tests for continuous releases

The study of the tests mentioned in table 14 suggests the following remarks:

- Only the Tortoise Desert and Goldfish tests involved two-phase releases ;
- The liquid release tests on water (Burro, Coyote and Maplin Sands) do not offer any conclusions for ammonia which has a very different behaviour with water ;
- Of the tests, only those at Thorney Island used obstacles.

The information obtained from these tests, in terms of dispersion, relates to general aspects. Within the scope of these tests, it is not possible to account for the specificity of ammonia, such as jet formation, aerosol generation, reactions with air moisture, etc.

3.2.10.1 Summary

The atmospheric dispersion tests already completed have demonstrated:

- the influence of weather conditions ;
- the behaviour of ammonia which is dispersed like a heavy gas when it is released from a pressurised tank (no upward dispersion) ;
- a release impacting the ground made it possible to collect 70% of the ammonia released (Unie van Kunstmest Fabrieken bv tests, Netherlands, 1972).

However, data is particularly lacking on:

- the characterisation of the source term of the release and the formation of the two phase jet in the case of pressurised releases and particularly aerosol generation and progression;
- release tests impacting a surface with higher flow rates. The tests such as the Unie van Kunstmest Fabrieken bv tests, Netherlands, 1972, did not study ammonia dispersion. These tests just studied the phenomenon in a qualitative manner.

3.3 MODELLING OF ATMOSPHERIC AMMONIA DISPERSION

As seen in the previous section, modelling particularly needs to account for:

- gravitational effects due to the cloud temperature ;
- the presence of aerosol ;
- reactions with air moisture.

Different types of dispersion models exist: Gaussian models, integral models and three-dimensional models. These models are described extensively in the literature, e.g.: CCPS (1999) or RIOU (1989).

3.3.1 Gaussian models

Purely Gaussian models are, in the majority of cases, unsuitable for the detailed modelling of pressurised liquid ammonia releases. In fact, ammonia does not behave like a passive gas in the initial release phases.

3.3.2 Three-dimensional models

Three-dimensional models make it possible to solve the physical equation system governing atmospheric dispersion directly. In this way, a large number of situations of varying complexity can be simulated. However, this requires precise incorporation of all phenomena such as, for example, atmospheric turbulence, site topography or obstacles.

These models are more complex to implement and require qualified personnel for their use. The limitations of these models include the choice of turbulence models, mesh refinement or convergence criteria. For this reason, more simple digital models are used more frequently.

3.3.3 Integral models

Half-way between Gaussian models and three-dimensional models, integral models give interesting results with shorter implementation times than three-dimensional models. They make it possible to account for the specificities of the gas and release in the initial phase, until the dispersion becomes passive.

However, such programs do not account for obstacles such as buildings, topography and vegetation. Only a roughness parameter can be used to modulate the results according to the average site configuration.

3.3.4 Residual problems and improvements to be made

Lantzy (1992) states that it should be borne in mind that the purpose of atmospheric release modelling is to predict, as accurately as possible, the effects of a release of hazardous substance. For this purpose, the characterisation of the source term is decisive, because the best dispersion models will always give incorrect results if the source term is incorrect.

Some points presented in this article may be repeated for the study of ammonia dispersion, more specifically for the study of the source term for ammonia releases. These points relate to two-phase flows, aerosol formation and progression and pool formation and evaporation.

3.3.4.1 Two-phase flows

With respect to two-phase flows, according to Lantzy (1992), future research should focus on:

- improved understanding of the effects of non-equilibrium for releases via small tubes (less than 100 mm long). This is the scope of interpolation between flows in genuine non-equilibrium and homogeneous flows ;
- a more accurate determination of the discharge coefficient. This value is generally between 0.6 and 1.0 and, for this reason, has a significant influence on the calculated flow rate ;
- the creation of an experimental database for ruptures of pipes with a high L/D ratio. To date, the research carried out in this area has been limited to computer simulations. Data is required to verify and extend the existing theories ;
- the development of entrainment and mixing models for disaster-related ruptures. For example, there is no entirely satisfactory theory to estimate the drop size and release velocity correctly. Large-scale data is required to complete the small-scale data currently available.

3.3.4.2 Aerosol formation and progression

To model releases from pressurised storage tanks correctly, the models must account for the aerosol and the progression of the droplets along the jet. However, for this, it is necessary to be able to estimate the initial size of drops and their distribution accurately. Therefore, most of the research to be developed relates to:

- droplet evaporation. It is necessary to predict the quantity of the substance that will be transported correctly ;
- droplet coalescence ;
- the effects of viscosity on shearing. No data is available to date ;
- release orifice non-uniformity.

3.3.4.3 Pool formation and evaporation

Pool formation and evaporation is a subject which should be examined in order to understand and model the phenomena liable to be encountered during accidents. In particular, the following points must be studied:

- freezing of ground moisture. This phenomenon affects thermal conduction towards the pool. It is not very clearly understood at the present time ;

- infiltration of substances into the ground. For a cryogenic substance (such as ammonia), this phenomenon increases the contact surface area which favours heat transfer and, for this reason, the evaporation rate. For a non-cryogenic substance, this phenomenon results in a pool with a smaller surface area and less evaporation. As for the above point, this phenomenon is not well known ;

- the effect of the substrate on pool size. There are no good theories linking the roughness of the substrate and the pool size directly for a smooth and irregular surface (i.e. in the majority of actual cases) ;

- evaporation with light winds. Data would be required to develop suitable models for these conditions.

In addition, with respect to the evaluation of source term models, Lantzy (1992) points out that, generally, the evaluation is not conducted on the source term model itself, but on the combination of the source term model and dispersion model.

Lantzy also specifies that most of the data available relates to distances of over 300 m. Well-designed and well-instrumented tests are required in the vicinity of the release point so as to compile quality data for the source term model evaluation.

In conclusion, Lantzy expresses the need for satisfactory experimental data for the evaluation and development of all the aspects of source term modelling.

3.3.5 Summary

In sum, a number of technical problems still need to be dealt with in detail in various areas relating to the study of atmospheric pollutant dispersion.

With respect to source term comprehension and modelling, it is necessary to examine in detail:

- the two-phase release ;

- pre-mixing in the jet phase ;

- aerosol formation and behaviour in dispersion.

With respect to the specificity of ammonia:

- density ;

- reactions with air moisture.

With respect to the extrinsic conditions for the release:

- definition of weather conditions (wind profile, temperature gradient, hygrometry, etc.) ;

- topography and orography ;
- influence of roughness.

With respect to problems directly associated with modelling:

- limit conditions with the choice of closing equations for three-dimensional models ;
- influence and importance of the different empirical settings for simplified models and the suitability of these settings with respect to reality ;
- influence of the software user on modelling results.

3.4 ISSUES EXAMINED IN THIS PROGRAMME

This research programme particularly consists of completing knowledge on atmospheric ammonia dispersion in open environments and in obstructed environments and making comparisons between results obtained by means of digital models and measurements made during tests. To this end, a large-scale test programme was initiated.

It aims to provide solutions for the problems raised in the previous chapter, more specifically on the two points presented below.

3.4.1 Impacting jets

Within the scope of an ammonia release study, it is difficult to characterise the source term correctly, particularly the quantity flowing and forming a liquid pool, referred to as the "rain-out" in the literature.

To try to understand large-scale phenomena, INERIS used ammonia releases in configurations differing only by the presence of obstacles in the very near field:

- two-phase jet in open field ;
- two-phase jet impacting a wall at a distance of less than 3 metres ;
- two-phase jet impacting the ground.

The difference between these types of release should make it possible to estimate the pool formation rate. This potential pool formation in the case of an impacting jet will enable a more realistic approach within the scope of safety studies.

Tests conducted on gaseous jets impacting a surface have demonstrated that, under test conditions, the volume for which the concentration is greater than a given concentration was much higher than in the case of a free jet, up to 10 times greater during tests with methane (Chaineaux, 1995). In fact, when the jet impacts an obstacle, the air entrainment is, in principle, reduced as the cloud tends to be "diluted" with gas-charged air.

If this result is confirmed, it will be necessary to take this aspect into account for safety in the near field.

However, an impacting jet may result in the formation of a pool on the ground and, therefore, reduce the gas flow rate passing in the atmosphere. The distances corresponding to a given concentration may then be less than those that would be obtained in the case of an open field release.

Facility safety studies characterised by a configuration similar to these tests will be more realistic if these phenomena are taken into consideration.

3.4.2 Influence of orifice geometry

Within the scope of the safety studies, releases are generally considered to be circular (due to guillotine pipe rupture).

In this programme, two-phase releases via different orifices, but with the same open cross-section surface area, were used, in order to compare the results obtained in terms of concentration leeward from the mission.

The reference orifice is a circular orifice (nozzle). Then, an orifice formed by a flange in which the seal was removed beforehand and replaced by blocks of the same thickness was produced as shown in figure 2 below.

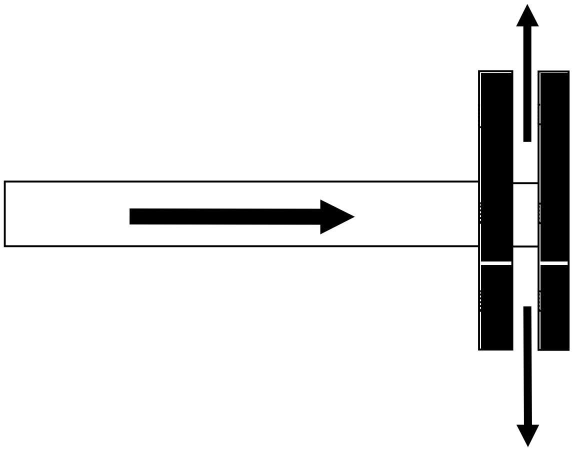


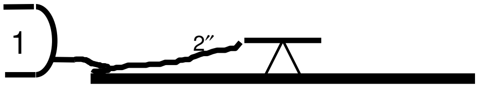
figure 2: Diagram of device used to simulate a leakage on a flange.

4. DESCRIPTION OF LARGE-SCALE TESTS

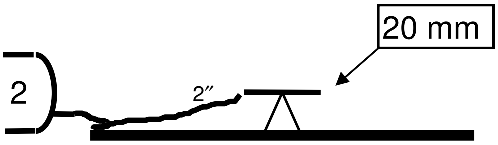
In this research programme, fifteen large-scale ammonia dispersion tests were conducted. In order to obtain configurations similar to industrial situations, the tests were defined with the 6 industrial firms taking part in the programme.

4.1 PRESENTATION OF TESTS CONDUCTED

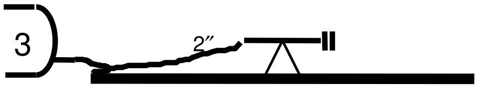
The fifteen release configurations produced during this test campaign are described briefly below next to each of the block diagrams. These tests are numbered from 1 to 8 b in the chronological order in which they were carried out. For each of these configurations, the pipe diameter is 2 inch (50.8 mm). Unless specified otherwise (case of tests 2, 3, 4p and 2b), the circular orifice also has a diameter of 2 inch.



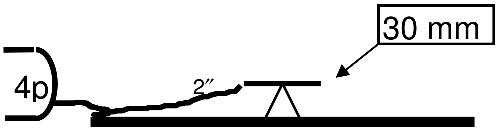
Horizontal release at a height of 1 metre in gaseous phase. Only test conducted in gas phase. The subsequent tests all relate to ammonia releases initially in liquid phase.



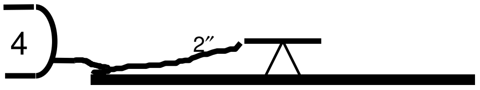
Horizontal release at a height of 1 metre in liquid phase via a 20 mm orifice.



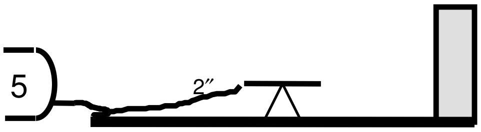
Release via a 2 inch flange at a height of 1 metre. The distance between the two parts of the flange is 1.6 mm such that the release surface is equal to 18 mm.



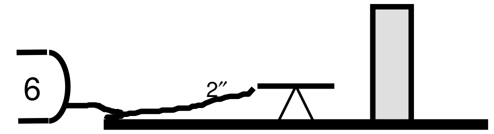
Horizontal release at a height of 1 metre via a 30 mm orifice.



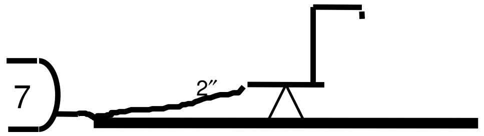
Horizontal release at a height of 1 metre.



Horizontal release at a height of 1 metre impacting a wall with a surface area of 3 m x 3 m. This wall is located 3 m from the end of the release system.

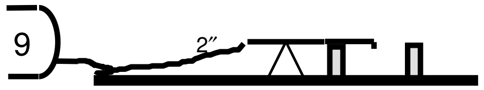


Horizontal release at a height of 1 metre impacting a wall with a surface area of 3 m x 3 m. This wall is located 1 m from the end of the release system.

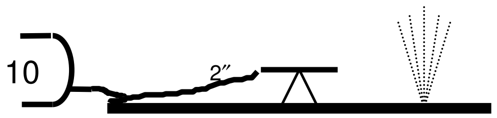


Vertical release impacting the ground from a height of 3 m.

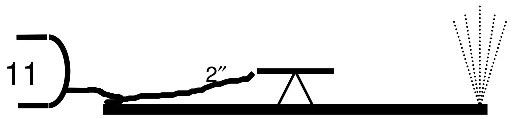
Vertical release impacting the ground from a height of 1 m.



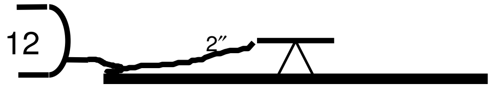
Vertical release impacting the ground from a height of 1 m in a retention dike with a surface area of 2 m x 2 m and 1 mm high (4 m^3).



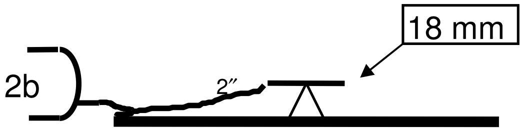
Release identical to release No. 4. A water curtain located 25 m from the release point was started up during the test.



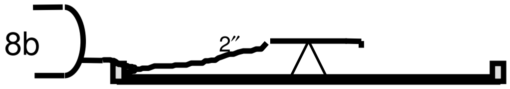
Release identical to release No. 4. A water curtain located 60 m from the release point was started up during the test.



Release identical to No. 4. The temperature of the liquid ammonia inside the tank was lowered to -12°C before the test.



Release identical to No. 2 with a 18 mm diameter orifice.



Vertical release impacting the ground from a height of 1 m in a retention dike with a surface area of 10 m x 10 m and 5 cm high (5 m^3).

4.2 DESCRIPTION OF TEST RESOURCES

To conduct these large-scale ammonia dispersion tests, the CEA-CESTA (*Centre d'Etudes Scientifiques et Techniques d'Aquitaine*, Centre of Scientific and Technical Studies of Aquitaine) Outdoor Testing Site (TEE) was selected. It is located approximately sixty kilometres south of Bordeaux. The site covers a surface area of 950 hectares. It is completely enclosed and access to it is continuously monitored. The safety study conducted demonstrated that the tests envisaged could be carried out under satisfactory safety conditions particularly due to the space available.

The TEE test site is completely flat and free from any obstacles. At the centre of this site, which has a radius of approximately two kilometres, there is a square concrete slab with 10 metre sides and approximately 15 cm thick. The releases were produced from this slab.

4.2.1 Description of release point

In the immediate vicinity of the release slab, three ammonia tanks, of 12 m^3 each, were set up. The liquefied ammonia was stored in the tanks at its saturating vapour pressure. The dimensions of the tanks were as follows:

- total length: 4810 mm
- shell length: 3700 mm
- internal diameter: 1874 mm
- maximum liquid height: 1500 mm

During the tests, only one of these tanks was connected to the release system located at the centre of the slab, which was equipped with 5 thermocouples and a pressure sensor, in order to monitor the progression of the pressure and temperature conditions inside the tank during each test.

The 5 thermocouples were installed on a vertical line from the base of the tank at the following heights:

- 50 mm
- 400 mm
- 750 mm
- 1100 mm
- 1450 mm

The pressure sensor was located at the top part of the tank, in the gaseous phase. This sensor is referenced P3 in figure 3 overleaf.

The tank was also connected to a nitrogen bundle used either to pressurise it or to keep the pressure constant during a test, or to purge, after a test, the pipe connecting it to the release system.

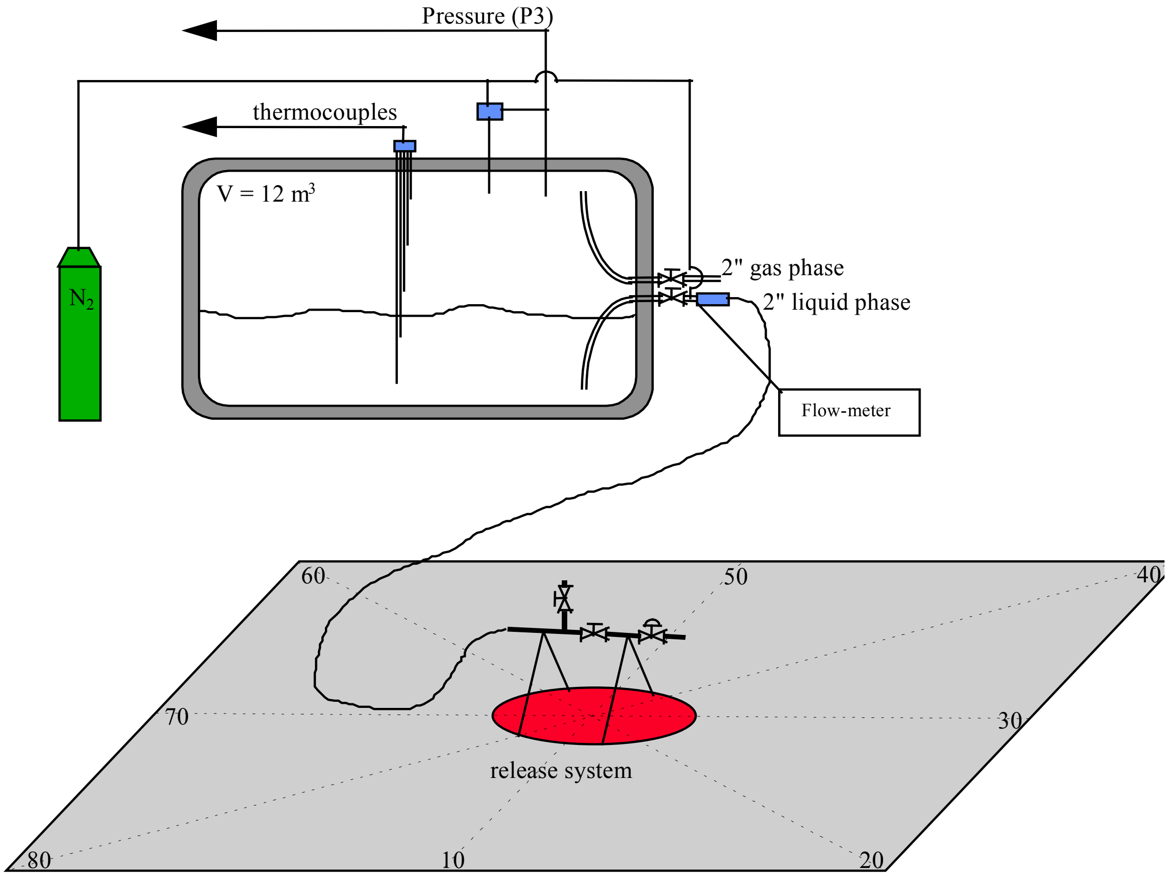


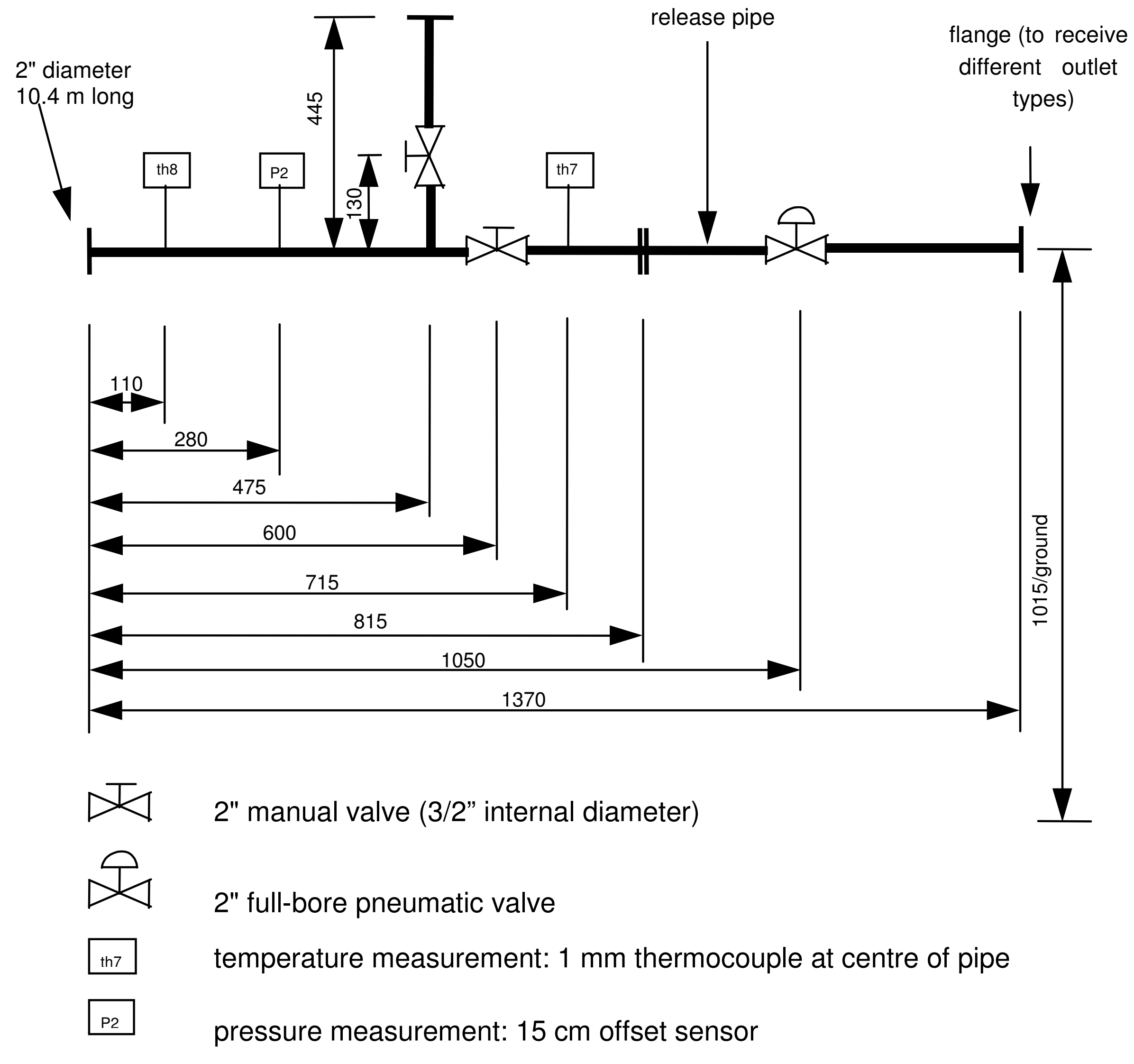
figure 3: release point diagram

To produce the fifteen releases defined within the scope of this programme, the two 2 inch diameter manual valves installed on the tank were used: one was connected to the gas phase and the other to the liquid phase. This two identical valves are not full bore and their bore diameter is 3/2 inch.

After the 2 inch valve connected to the liquid phase, a 300 mm long and 41 mm internal diameter flow-meter was installed. Intended to operate in liquid phase, it did not give any interpretable results during the tests as the ammonia was two-phase from the valve located just upstream for almost all the tests.

The connection between the flow-meter and the release system was provided by a 50 mm diameter and 10.4 m long pipe.

Finally, the release system consisted of a 2 inch pipe instrumented with valves, thermocouples and pressure sensors (see figure 4 overleaf).



Note: all the distances are given in mm.

figure 4: description of release system

The axis of the release system was located 1015 mm above ground level.

The end of the release system was equipped with different types of outlets (see figure 5) according to the desired test configuration.

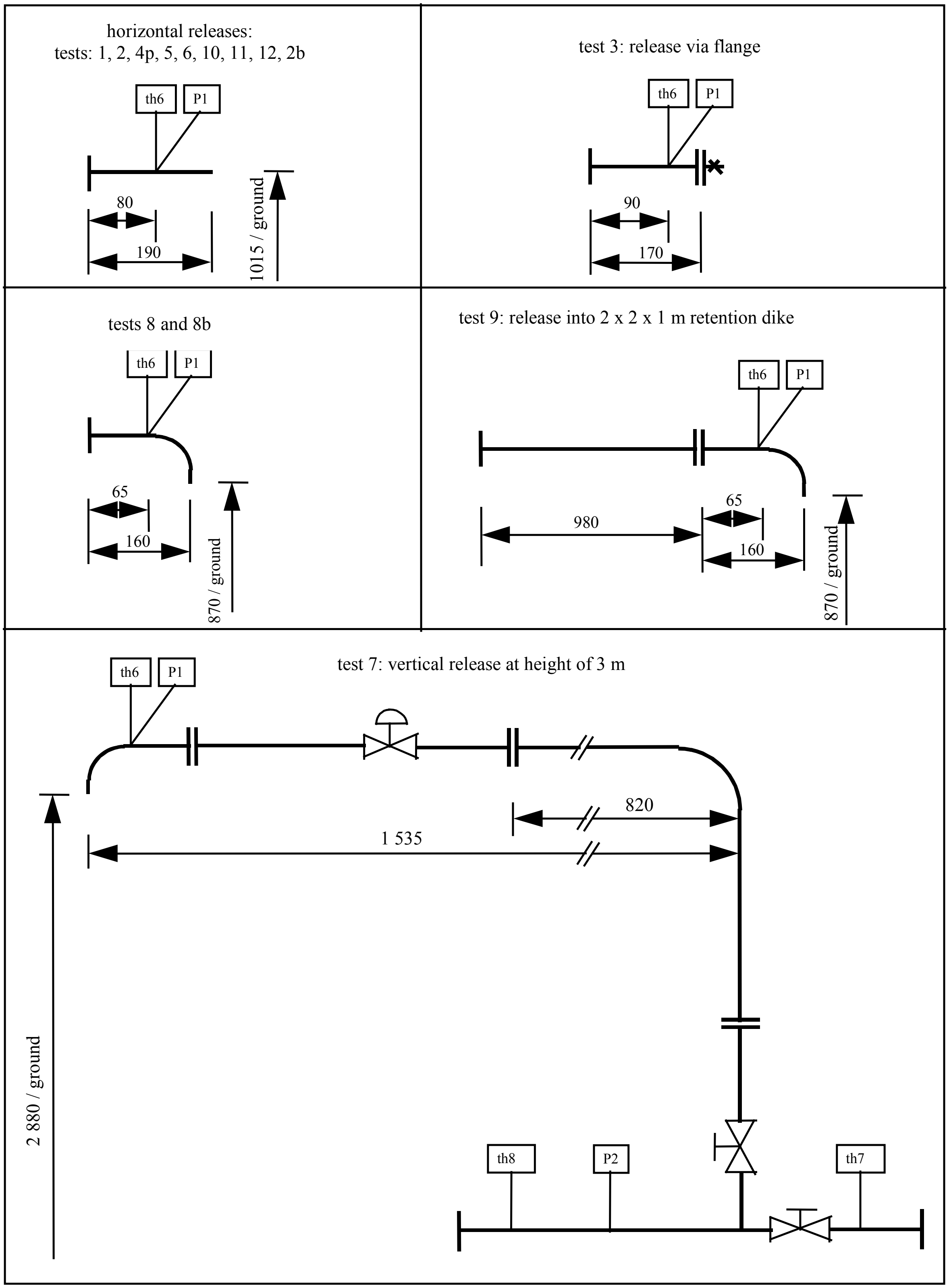


figure 5: different outlet types for each configuration

For the tests in which the jet was pointing towards the ground, the concrete slab surface was instrumented with thermocouples. For the jets against the wall, the slab was also instrumented with thermocouples. The instrumentation installed and the references of the thermocouples are described in appendix 1

photo 1: horizontal release impacting a wall

In the case of tests 2, 4p and 2b, the end of the release system was equipped with a 50 mm pierced cap of a diameter corresponding to the test, i.e. 20 mm, 30 mm and 18 mm for these three tests, respectively.

For test 3 with the flange, the seal was removed. The thickness between the 2 parts of the flange was 1.6 mm. This is equivalent to a leakage surface area of 255 mm^2. Therefore, the equivalent surface diameter is 18 mm.

For tests 10 and 11, water curtains were produced with "peacock tail" hoses. The characteristics of these peacock tails were as follows:

feed diameter:	70 mm ;
feed pressure:	8 bar ;
water flow rate:	1200 l/min ;
x span:	32 m ;
y span:	10 m.

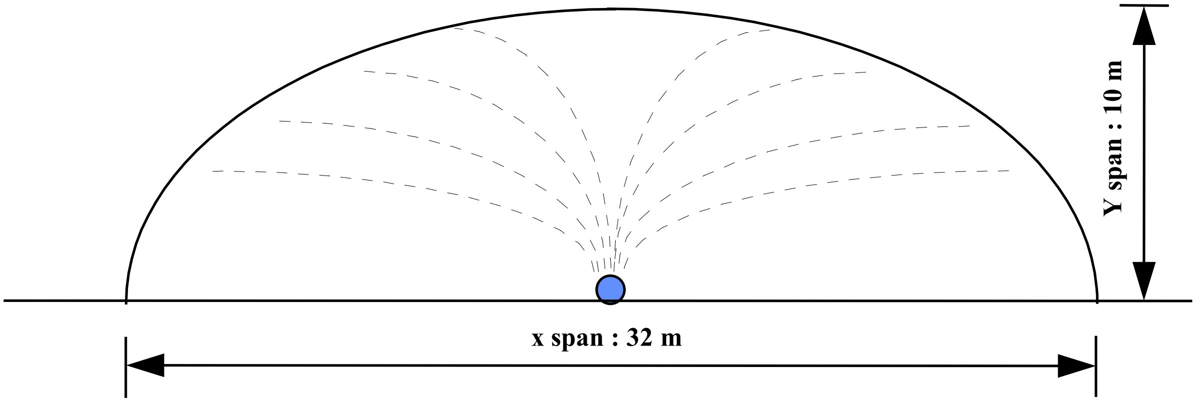


figure 6: spans of peacock tails used for tests 10 and 11.

For these two tests, two peacock tails were installed as described in figure 7 below.

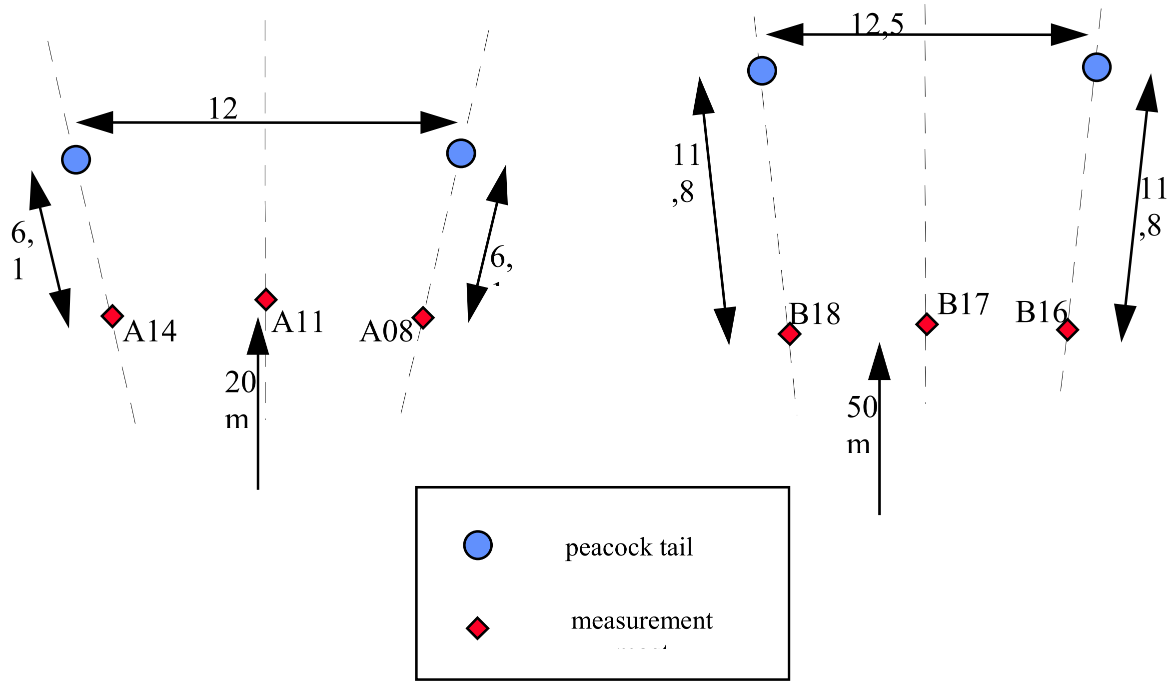


figure 7

Test 10: Layout of both peacock tails 25 m from release point.

Test 11: Layout of both peacock tails 60 m from release point.

The measurement mast position is specified in detail further in this report.

4.2.2 Weather measurement equipment

To measure the atmospheric conditions, a 10-metre high weather mast was set up 350 metres from the release point in the direction noted as 3 (reference M in figure 11). It consisted of three vane anemometers, located at a height of 1.5, 4 and 7 metres, a weather-cock at 7 metres and an ultrasonic anemometer at 10 metres.

A weather station was also set up next to the control station where the temperature, relative humidity and solar flux measurements were made. These measurements were made at a height of 1.5 metres. The acquisition frequency of these parameters was 1 Hz, except for the ultrasonic anemometer, which had a frequency of 10 Hz.

The type of equipment used is described below:

- 1 PULSONIC 429 weather-cock ;
- 3 PULSONIC 438 vane anemometers ;
- 1 PULSONIC CM6B pyranometer (solar flux measurement) ;
- 1 PULSONIC temperature probe ;
- 1 PULSONIC hygrometer ;
- 1 METEK – USA-1 ultrasonic anemometer.

An installation diagram is given in figure 8 below.

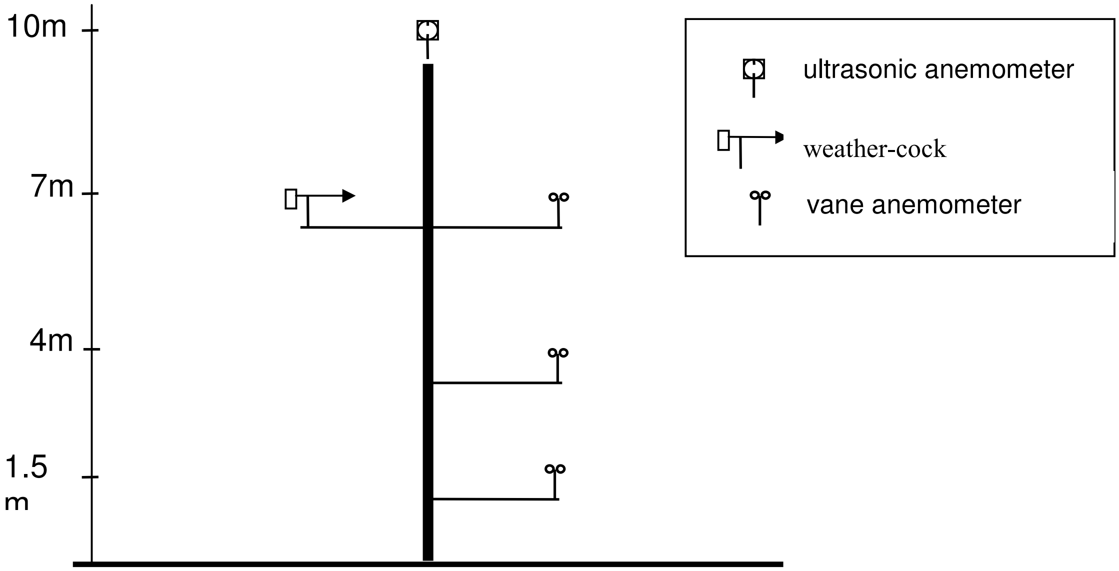


figure 8: Weather mast

The ultrasonic anemometer was installed with the x axis facing north and the y axis facing east.

The weather-cock was facing the opposite direction to the ultrasonic anemometer.

4.2.3 Ammonia measurement chain composition and tests

To conduct the large-scale tests, INERIS chose to use a standalone measurement chain both to minimise wiring, and also to be easy to move according to weather conditions (particularly wind direction variations). For this reason, the sensor electrical power supply was provided by batteries and cells. For each series of measurements, the data was stored on "EEPROM[5]".

In this way, the ammonia measurement chain consisted of an electronic unit on which it was possible to connect up to 4 sensors with different technologies. In total, 70 identical electronic units were produced for this programme.

An electronic unit comprises three parts arranged on an assembly plate inside an airtight housing:

- An electronic signal acquisition card, used to amplify the signal, perform the digital processing, display various parameters, program the configuration and save data. The main component of the card is a microcontroller specially adapted for the instrumentation.
- An EEPROM saving device designed for the primary acquisition of the data from the sensors in digital signal form (8192 data items).
- An electrical power supply (cells) to power the electronic circuits

The electronic card is equipped with an internal clock which starts up and shuts down the system at set times. During this period, the EEPROM saves the sensor measurements at a predetermined rate. For the tests, a 0.25 Hz frequency was selected, i.e. one measurement every 4 seconds, which made it possible, in view of EEPROM capacities, to save for 8 hours. At the end of each day of tests, the data collected and stored in the EEPROM was copied to a PC hard disk via a specific interface.

To select the sensors to be installed on the 70 electronic units, the releases envisaged in section 4.1 were modelled using atmospheric dispersion software. Some general information was obtained from these simulations:

- In principle, it is not necessary to fit sensors capable of measuring concentrations above 1% gaseous ammonia beyond 300 metres from the release point on the plume axis ;
- however, up to 200 metres from the release point, the sensors located on the plume axis should all be subject to concentrations above 1% ;
- finally, beyond 750 metres, the calculated concentrations are below 0.1%, i.e. 1000 ppm.

These results were considered as orders of magnitude and were adjusted according to the progress of the programme.

In this way, the sensors were selected according to the concentration to be measured, which is associated with the distance to the release point leeward from

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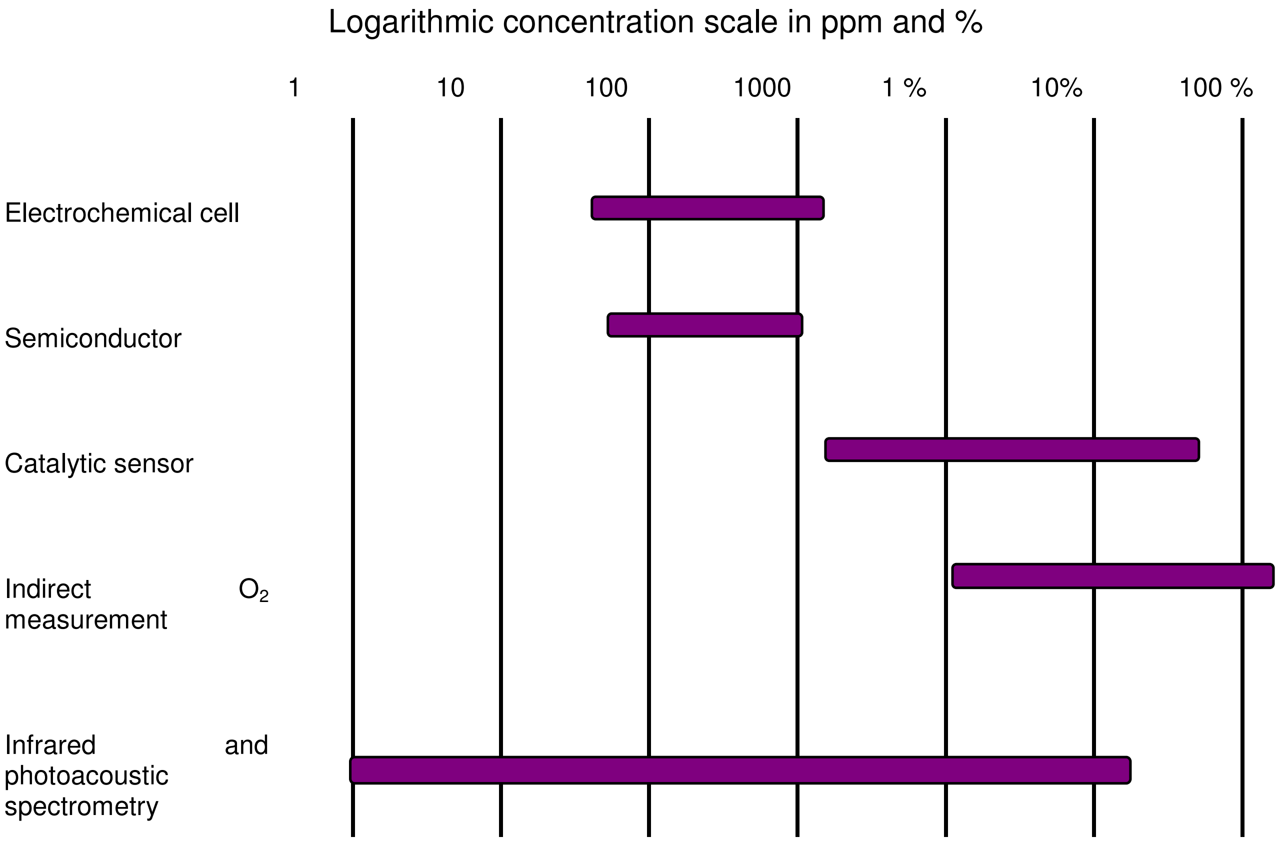
[5] EEPROM: Electrically Erasable Programmable Read Only Memory

the emission and the distance to the plume axis.

Several ammonia concentration measurement techniques could be envisaged, such as:

- electrochemical cells ;
- semiconductors ;
- catalytic sensors including pellistors ;
- indirect ammonia measurement by measuring oxygen in the air, based on the paramagnetic properties of oxygen ;
- measurement in infrared (IR) ;
- chromatography.

Each of these techniques applies to a specific concentration range as shown in figure 9 below. The concentration ranges are orders of magnitude which can be extended according to the characteristics of the sensors.



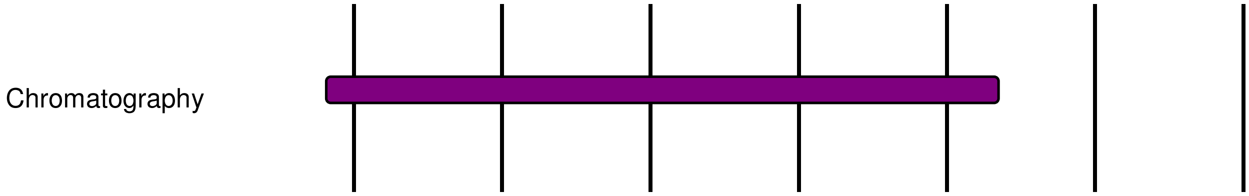


figure 9: Representation of specific concentration ranges for sensors

Appendix 2 describes the operating principle of the first three techniques mentioned above, which are the most widely used for combustible gas measurements.

Finally, the sensors, which were connected to the electronic units during the test campaign, are:

- pellistor type catalytic sensors, specific for ammonia (EEV VQ 41) used to measure ammonia concentrations between 0.1% and 15% (between 1000 ppm and 150,000 ppm). These sensors, 60 in number, were placed in the near field (up to 200 metres from the release point) ;

- electrochemical cells (SENSORIC NH3 3E 1000) measuring ammonia concentrations between 10 and 1000 ppm. These sensors, 50 in number, were arranged in the far field (200 metres to 1700 metres from the release point) ;

- 60 thermocouples (K type, 1 mm diameter, class 1, stainless steel sheath, 5 m long), used to measure temperature fluctuations. These thermocouples were installed next to each catalytic sensor up to a distance of 100 metres from the release point, particularly in order to assess temperature variations in the jet.

The EEV VQ41 pellistors and the SENSORIC NH3 3E 1000 electrochemical cells first of all underwent a series of laboratory tests at INERIS in order to verify their characteristics. The behaviour of these sensors was then tested at INERIS in a 50 metre long gallery with a 10 m^2 cross-section. Releases via 0.5 mm to 8 mm diameter orifices were carried out for these tests and made it possible to validate the measurement chain (Bouet, 1996).

To facilitate data processing, the microcontroller was programmed to supply the data directly in the unit (ppm vol.) and in the scale corresponding to the sensor. The data was stored in EEPROM as follows:

- electrochemical cell: in 10 ppm intervals up to 2000 ppm ;

- pellistor: in 250 ppm intervals from EEPROM value 0 to 130, and then in 560 ppm intervals from EEPROM value 131 to 255 ;

- thermocouple: in 0.3125℃ intervals, from -40℃ to +40℃.

Finally, a programme used to read and backup the data saved by the EEPROM was developed based on Labview software. A processing tool for this data was also developed based on this software.

4.2.4 Sensor instrumentation on test site

To enable easier installation of the electronic units before a release, the test site was also equipped beforehand with 150 x 3 m high masts. These masts offered the possibility of attaching the sensors at 4 different heights, i.e. 0.1, 1, 2 and 3 metres. They were arranged on 7 arcs 180° in amplitude centred on the release slab, with radii of 20, 50, 100, 200, 500, 800 and 1700 metres. On the first two arcs located at 20 and 50 metres, 41 masts were installed every 4.5°, and on all the arcs, 21 masts were installed every 9°.

To enable easier subsequent processing of the tests, the masts installed on the test site were identified by a **letter** and a **number**.

photo 2: Masts installed on the tests site

The **letter** corresponds to the radius of the arc, i.e. the distance from the release point (see table 15).

distance from release point (m)	20	50	100	200	500	800	1700	4	350	650
letter	A	B	C	D	E	F	G	S	M	T

table 15: Correspondence between distance from release point and associated letter.

The last three distances of 4, 350 and 650 metres identified in the above table correspond to the sensors installed on the release slab, the weather mast and a 19 metre high mast, respectively. In the case of the latter, from test 8, two electrochemical cells are installed at heights of 6 and 10 metres.

The **number** corresponds to a direction from the release point. We defined 80 directions, i.e. an angle of 4.5° between each. In the selected configuration, the north corresponds to the direction 50 (see figure 10). The layout of the masts was carried out in the directions between 1 and 41.

The numbering of the angles from the release slab is given in figure 10 below.

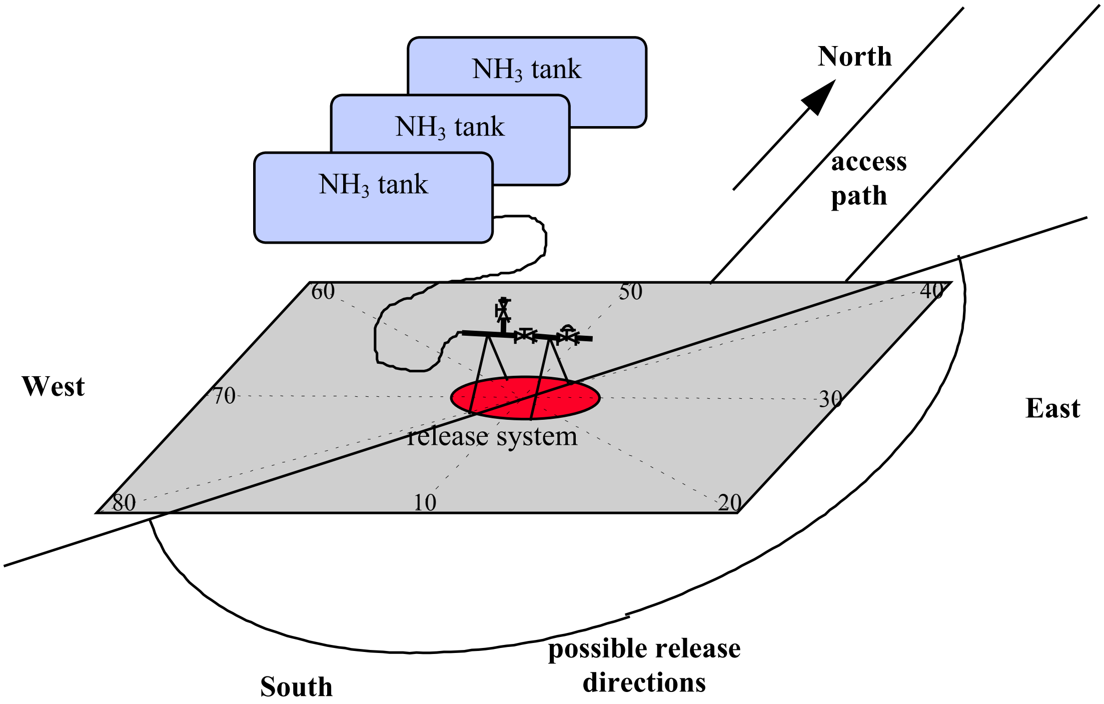


figure 10: Identification of angles on release slab

The numbering of the angles on the test site and the position of the masts are given in figure 11 below.

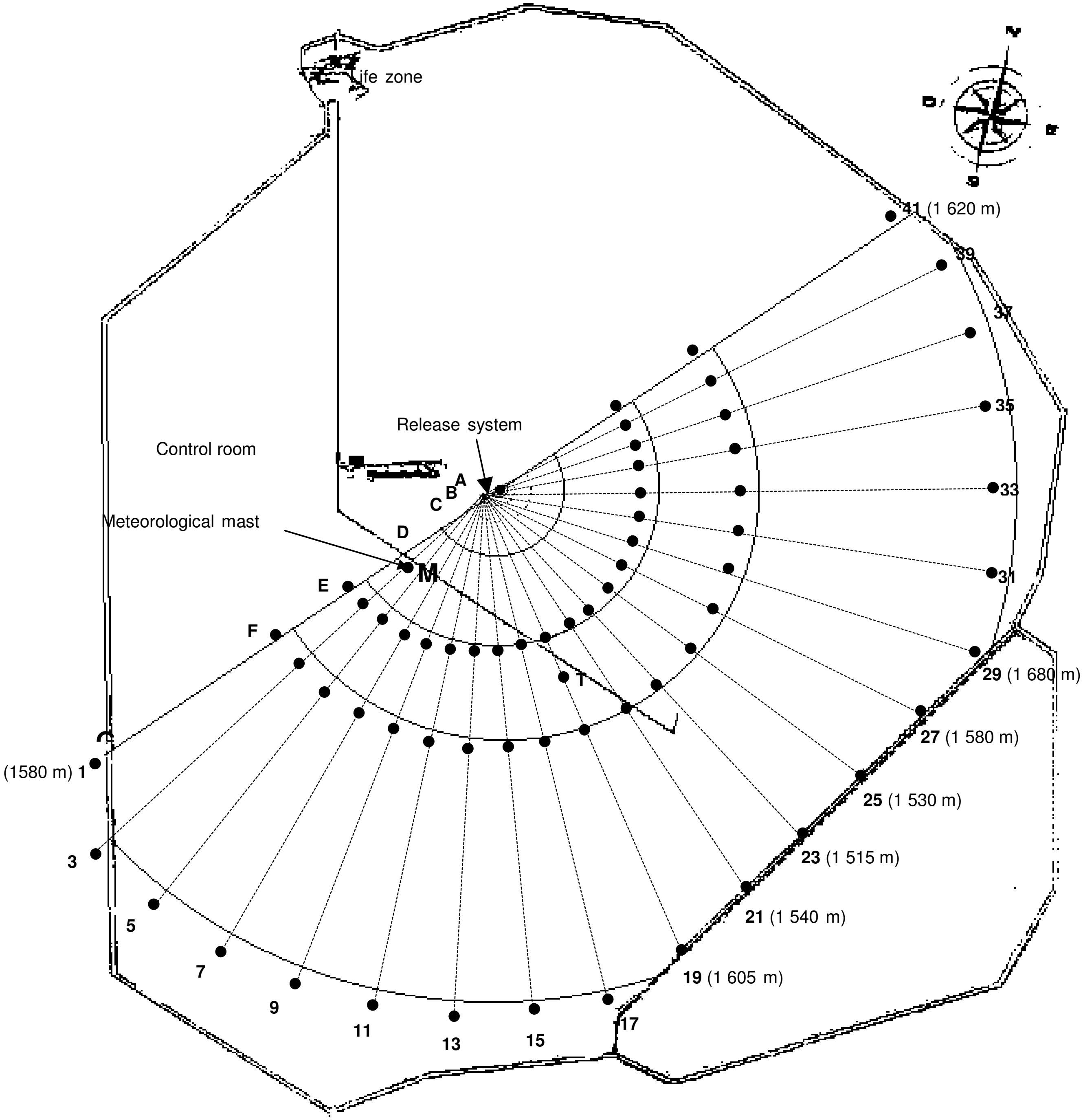


figure 11

Due to the favourable wind direction identified during the initial weather data analysis and the test site configuration, the measurement field defined in principle was located between the directions numbered 1 to 41.

The arc at 1700 metres is limited by the dimensions of the test site for the directions 1, 19, 21, 23, 25, 27, 29 and 31. For these directions, the distance at which the masts were positioned is given in brackets.

In each test, the sensors were installed on measurement masts in their final position leeward from the release approximately 1 hour before the start of the test. In this way, the sensors were all distributed along each side of the release axis on an angular sector ± 35° on either side of the axis.

For the impacting releases and the release via the flange, the sensor distribution angle was greater for the arcs located at 20, 50 and 100 metres (up to 80° on either side of the release axis). In these configurations, sensors were also added to the concrete slab over a 4-metre radius.

4.2.5 Acquisition equipment

The data collected during these tests was saved or processed by three separate types of acquisition equipment for the following points:

- the electronic units (measurement chain described in section 4.2.3) used for the acquisition, firstly, of ammonia concentration values using catalytic sensors and electrochemical cells connected to them and, secondly, temperature values measured via thermocouples which were also connected to them ;
- the LabView acquisition system for the weather sensors and for the pressure sensors located on the release point ;
- acquisition system for the thermocouples located on the release point, i.e. the thermocouples arranged in the tank, on the release system and on the ground or concrete blocks (acquisition by scanning).

The acquisition system for the data from the weather sensors and the pressure sensors was installed in the control station, in order to monitor the parameters during the test, at the same time as the acquisition, in particular:

- the pressure in the tank ;
- the pressure at the centre of the release system ;
- the pressure at the release orifice ;
- the wind velocity ;
- and the wind direction.

The location and acquisition frequency for each of these sensors are given in table 16 below.

sensors	distance from release point (m)	*θ*(°) – dir No.	z (m)	acquisition frequency (Hz)
vane anemometer	350	*211.5* - 3	7	1
vane anemometer	350	*211.5* - 3	4	1
vane anemometer	350	*211.5* - 3	1.5	1
ultrasonic anemometer	350	*211.5* - 3	10	10
weather-cock	350	*211.5* - 3	7	1
tank T (50 mm)	release system		0.05	0.2
tank T (400 mm)	release system		0.4	0.2
tank T (750 mm)	release system		0.75	0.2
tank T (1100 mm)	release system		1.1	0.2
tank T (1450 mm)	release system		1.45	0.2
pipe T (th8)	release system		1	0.2
pipe T (th7)	release system		1	0.2
orifice T (th6)	release system		1	0.2
thermocouples 11 to 30	Ground and obstacle			0.2
solar flux	450	*270* - 70	1.5	1
relative humidity	450	*270* - 70	1.5	1
temperature probe	450	*270* - 70	1.5	1
ammonia sensors	Leeward from releases			0.25
tank pressure (P3)	release system		1.9	1
pipe pressure (P2)	release system		1	1
orifice pressure (P1)	release system		1	1

table 16: sensor position and acquisition frequency

4.2.6 Video equipment

To monitor the tests from the control station, five CEA-CESTA cameras were placed on the test site:

- one surveillance camera at a height of 30 metres located between the release point and the control station ;
- one camera located 10 metres behind the release point, at a height of 10 metres ;
- one camera located 40 metres behind the release point, at a height of 26 metres ;
- one camera located 1000 metres behind the release point in direction 33, at a height of 1 metre ;
- one mobile camera at a height of 1.5 metre, positioned perpendicular to the release direction.

4.2.7 Safety

To conduct these tests, the site was divided into four zones:

- the "forefront zone" where the releases were carried out ;
- the "support zone", which was located in a 200 metre radius around the release point ;
- the "control room", located 450 metres windward from the release point ;
- and the "living zone", located at the entrance to the site approximately 1400 metres from the release point.

Each person present on the site was equipped with a filtering mask. In the "control room", the personnel present wore "tyvec" clothing. Six people equipped with special clothing and an individual breathing apparatus were prepared to intervene in the "support zone". Two of these people were also equipped with a pressure suit to intervene in the "forefront zone", in particular, if required, in the cold ammonia cloud. This never occurred.

No personnel were present to the ammonia release outside the "control room", apart from the six people located in the "support zone".

The different teams working on the site communicated with radio equipment.

A shower system was set up at the entrance to the "forefront zone".

A medical service was available at any times next to the "control room".

5. RELEASE CONDITION MEASUREMENTS

In order to understand the atmospheric dispersion of a pressurised liquefied ammonia release, it is important, firstly, to determine the ammonia flow conditions in the pipe, and, secondly, to evaluate the weather conditions at the time of release correctly.

5.1 FLOW CONDITIONS IN PIPE

Initially, we will present the experimental conditions in which the releases carried out within the scope of this programme were conducted. Then, these release conditions are analysed.

5.1.1 Experimental release conditions

The experimental conditions under which the tests were conducted are frequently referred to as the "source term" of the release. The source term particularly specifies the flow rate, temperature, pressure, velocity and quality[6] values at the opening. In this programme, the measured source term values are essentially temperature and pressure values, along with the quantity of ammonia released.

During each test, the pressure and temperature conditions were measured and recorded continuously every second, both in the tank and at different points of the pipe (see chapter 4).

As an illustration, the two graphs in figure 12 below show:

- the typical progression of the pressure conditions in the tank and in the pipe during a release ;
- the progression of the temperatures located at different heights in the tank and located in the pipe.

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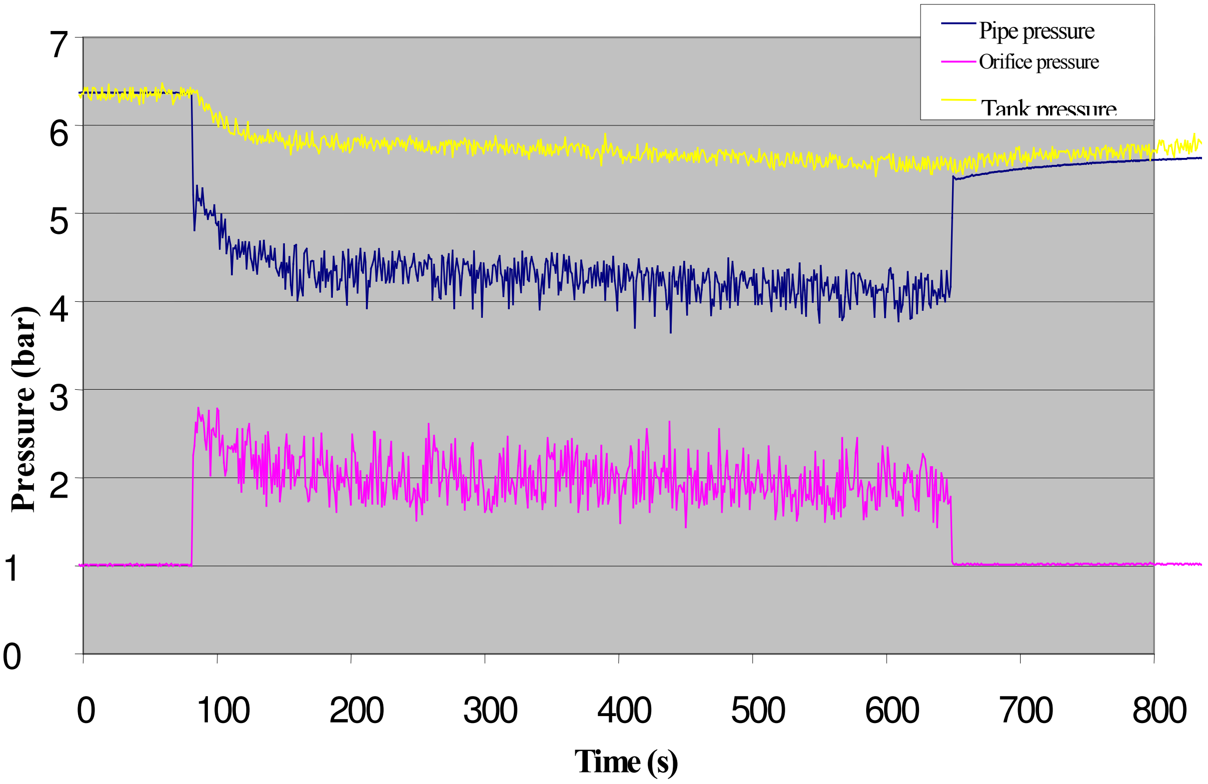
[6] release quality: a single-constituent two-phase flow is essentially characterised by its quality, i.e. the mass fraction of its vapour phase

These two graphs show the conditions measured and recorded during test 4.


Progression of pressure conditions (test 4)

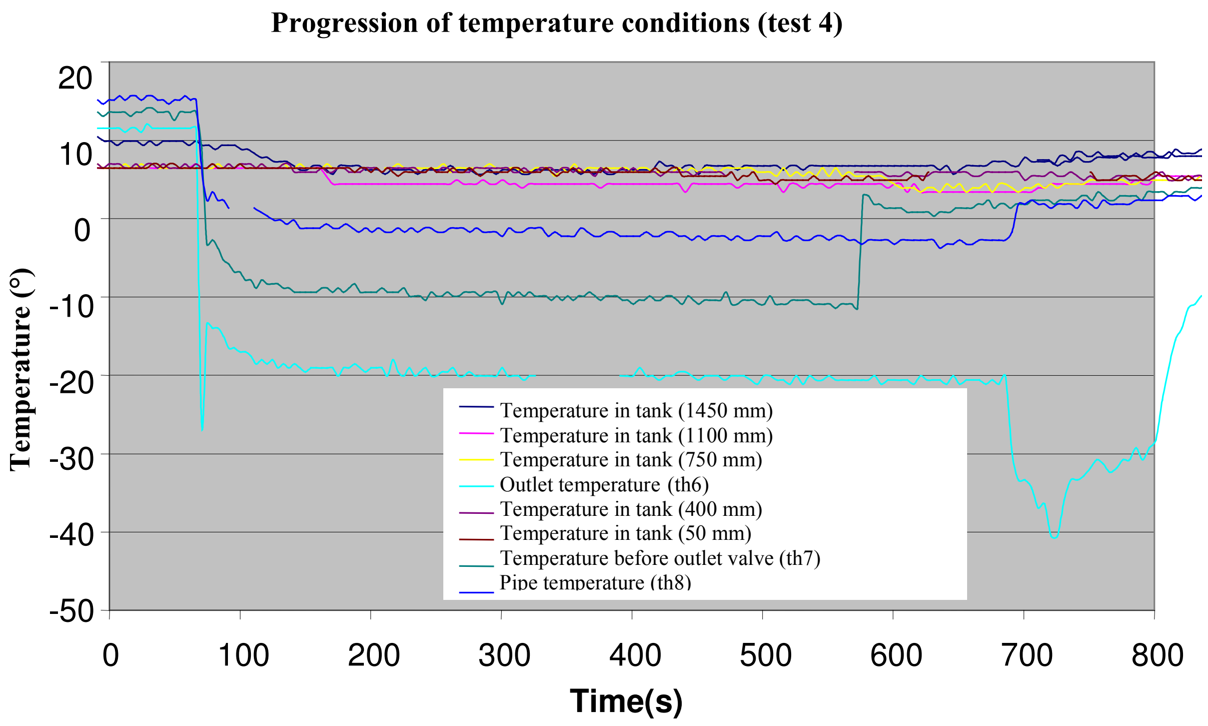

Progression of temperature conditions (test 4)

figure 12: Progression of pressure and temperature conditions in tank and in release pipe

For test 1, the gaseous release was produced from the vapour pressure inside the tank. The tank was then depressurised and the test was stopped when the pressure had reached approximately 1.8 bar absolute.

With respect to test 2, a 1 bar pressure surge was produced beforehand with nitrogen inside the tank. The nitrogen regulation system then kept this pressure constant throughout the test.

During test 3, via the flange, no nitrogen pressure surge was produced beforehand. However, the initial existing pressure in the tank was maintained throughout the test by means of nitrogen injection.

For all the subsequent tests, no nitrogen pressure surge was produced before the test and the pressure was not kept constant throughout the test. In this way, for each test, a varying pressure drop was observed in the tank according to the release conditions.

For each test, the behaviour of the pressure and temperature sensors was substantially the same. As a general rule, with respect to the values measured during the tests, it is possible to note that:

- inside the instrumented tank, the value of the temperature in the gaseous ceiling was identical to the temperature of the liquid ammonia from the second part of the night. On the other hand, after sunrise, temperature differences between the two phases could be observed. In this way, depending on the outside temperature, the sunlight and tank filling rate, the temperature of the gas phase sometimes increased more rapidly than that of the liquid phase. Maximum differences of 10℃ between the two phases were measured within the scope of this programme ;
- before a release, the value of the pressure in the tank rarely corresponded to the saturating vapour pressure of the liquid ammonia temperature. It was generally between the saturating vapour pressure corresponding to the temperature of the gaseous ceiling of the tank and the saturating vapour pressure corresponding to the temperature of the liquid ammonia depending on the time of day, the ambient temperature, the sunlight conditions and the tank filling rate. In some configurations, the difference between the pressure in the tank and the saturating vapour pressure corresponding to the temperature of the liquid ammonia was of the order of 1 bar ;
- in the case of a release in which the temperature of the gaseous phase was initially greater than the temperature of the liquid phase, a decrease in the temperature of the gas phase to the temperature of the liquid phase was conventionally observed. Depending on the initial and ambient conditions, the temperature was liable to fall rapidly after the start of the test, and then became equal to the temperature of the liquid phase ammonia during the test ;

- the pressure inside the tank, progressing under similar conditions to the gas phase saturating vapour curve, could, therefore, in the same way as the temperature values, change rapidly during the first minute depending on the time of day and sunlight conditions ;

- once the first minute of the release had elapsed, the pressure and temperature conditions inside the tank progressed in a constant and slower manner for the remainder of the release: drop of 200 to 400 mbar for a pressure of the order of 6 bar absolute, and 0.5 to 2°C temperature decrease ;

- while the ammonia was flowing in the pipe, a drop in pressure and, therefore, temperature was observed between the tank and the orifice. Typically, for a temperature value of approximately 10°C in the tank, the temperature at the orifice was approximately -15°C ;

- unlike the conditions in the tank during a test, the pressure and temperature conditions at the opening changed more significantly: on average, drop in pressure between 0.5 and 1 bar for an initial orifice pressure below 3 bar absolute, and decrease in orifice temperature between 5 and 10°C ;

- the pressure and temperature measurements made at the same point of the release pipe demonstrated that the pressure was similar to the saturating vapour pressure corresponding to the temperature measured at this point ;

- after the end of the release, since the valves were closed, the temperature and pressure values progressed more or less rapidly to their pre-test conditions, except for the pressure and temperature at the orifice. In fact, since the orifice is at atmospheric pressure, the liquid ammonia remaining at the orifice continued to be vaporised by lowering its temperature further.

During the tests, no satisfactory continuous flow rate measurement was made. Only the mean release flow rate value was estimated on the basis of the quantity of ammonia released and the release time.

The general characteristics of all the releases carried out are described in the table below.

Test No.	Release characteristics		
	Time (sec)	Quantity released (kg)	Mean flow rate (kg/s)
1	460	300	0.65
2	440	1980	4.5
3	540	1400	2.6
4 prel.	660	2380	3.6
4	600	2520	4.2
5	600	2520	4.2
6	600	2520	4.2
7	670	2560	3.8
8	875	3420	3.9
9	605	2370	3.9
10	690	2150	3.1
11	600	1800	3
12	660	2000	3
2b	720	1400	1.95
8b	780	2120	2.7

table 17 General characteristics of release conditions

5.1.2 Release flow condition analyses

When ammonia is stored in the liquid state at its saturating vapour pressure, its use generally results in a pressurised liquid flow in a pipe. In the event of a rupture on this pipe, the flow conditions are modified, with the ammonia changing from operating pressure and temperature conditions to conditions corresponding to atmospheric pressure and a temperature below that prior to the rupture.

These new conditions at the opening site must be determined in order to estimate the characteristics of the release, particularly the mass flow rate, the release rate, the release quality, pressure and temperature. These values form what is referred to as the "source term" of the release. The difficulty establishing the mass flow rate of the release at the opening particularly lies in the evaluation of the flow state in the pipe, If the liquid ammonia encounters a low pressure wave, it is vaporised. Ammonia is said to undergo a thermodynamic flash generating a mixture of liquid and vapour which affects the flow.

A distinction is essentially made between three different flow states, i.e.:

- bubble state: the liquid phase is continuous and contains gas bubbles ; in this case, liquid is in the majority ;
- annular or semi-annular state: the gas velocity is greater than that of the liquid against the walls of the pipe ;
- dispersed flow: the gas flow rate is high, the liquid is dispersed in the gas phase; in this case, the liquid is the minority phase in the mixture.

In order to determine the source term at the release point, it is necessary to understand and determine the characteristics of the flow in the pipe.

There are a large number of models used to describe the release in the case of ejection via a conduit. These models, mentioned for example by Langard (1995), Bigot (1996), U.I.C. (1987), can be classified into three categories in order of increasing complexity:

- homogenous equilibrium models (HEM) ;
- models with differences in velocity (between gaseous phase and liquid phase) ;
- non-equilibrium models.

In the homogeneous equilibrium models, the gas and liquid phases are assumed to:

- have the same velocity;
- be distributed homogeneously;
- be at the saturation temperature.

These assumptions imply that:

- the two-phase flow is considered as a homogeneous fluid with average properties between those of the gas and liquid ;
- the flow is at thermodynamic equilibrium (no heat or mass exchange takes place between the phases).

In addition, the flow is assumed to be stationary and one-dimensional.

There are two main categories of equilibrium models:

- *isentropic expansion models:* in this case, the entropy of the fluid subject to the expansion remains constant while its enthalpy decreases. In this case, the loss of enthalpy is assumed to be balanced by the gain in kinetic energy in the flow.
- *isenthalpic expansion models:* in this case, the enthalpy of the fluid remains constant while its entropy decreases. This loss is balanced by the friction energy applied by the flow.

Van den Akker et al (1983) demonstrated that these two assumptions are equally unrealistic but that the error generated in the "constant enthalpy" assumption is less significant.

The purpose of these models is to determine the flow rate at the opening. Within the scope of this programme, the tests conducted make it possible to determine the temperature and pressure at the opening and the mean flow rate throughout the test. A HEM model makes it possible to determine, in addition to these values, the quality of the flow at the opening. This parameter was not measured directly during the tests. A complete model, proposed by Wheatley (April 1987) and belonging to the HEM model category, is presented below and its results are compared to the experimental results obtained during the tests.

Modelling of flow rate at opening: Wheatley approach (April 1987)

The purpose of this modelling is to determine on the basis of the tank conditions (P_{int}, T_{int}):

- the pressure-temperature conditions at the opening ;
- the mass flow rate of the release ;
- the quality at the opening.

The basic hypotheses for this model are that:

- the fluid expansion is considered to be isentropic and stationary
- the two-phase fluid is considered to be homogenous and in liquid-vapour equilibrium

In this way, the model proposed is based on the following equations:

- entropy equation: $Cp_{liq.}Ln(T_{int}) = Cp_{liq.}Ln(T_b) + \frac{x.Lv(T_b)}{T_b}$ (1)

- Euler's equation: $\frac{Ub^2}{2} = \alpha_p^2 \left(\int_{Pb}^{P\,int} v.dP + g.h_{int} \right)$ (2)
- internal pressure equation as a function of temperature and liquid level:
  $P_{int} = P_{sat}(T) + \rho_{liq}.g.h_{int} = \exp\left(B_0 - \frac{A_0}{T}\right) + \rho_{liq}.g.h_{int}$ (3)
- Specific volume equation: $v = (1 - x).v_{liq} + x.v_{gas}$ (4)
- Clausius-Clapeyron's equation: $Lv(T)\ T(v_{gas} - v_{liq})\ \frac{dP_{sat}}{dT}$ (5)

After integration, Euler's equation is expressed as follows:

$$\frac{Ub^2}{2} = \alpha_p^2 \left(\frac{P_{int} - P_b}{\rho_{liq}} + Cp_{liq}(T_{int} - T_b) - Cp_{liq}.T_b.Ln\left(\frac{T_{int}}{T_b}\right) + g.h_{int} \right) \quad (6)$$

This expression is used to determine the velocity of the fluid at the opening as a function of the difference in pressure between the tank and the outlet. Since the fluid is assumed to be at saturation, the temperatures are known once the pressures are known.

The coefficient α_p is an empirical corrective factor used to account for the effects of friction; as a general rule, it is taken to be equal to 0.6 in the case of a wall opening and equal to 0.8 or 0.9 in the case of a pipe rupture.

The problem then consists of determining the pressure of the fluid at the opening. The existence of a pressure gradient between the tank and the opening induces a significant acceleration of the fluid, i.e. potential energy is converted into kinetic energy. The velocity of the fluid at the outlet will be limited by the propagation rate of the pressure waves in the fluid, i.e. the speed of sound.

It is accepted that, if the pressure gradient is sufficiently high, the fluid will reach the speed of sound at the outlet (May, 1996). If this is the case, the flow is said to be critical.

A critical (or sonic or blocked) single-phase flow is characterised in that a downstream decrease in pressure, below a certain threshold, has no influence on the flow. This pressure threshold is referred to as the "*critical pressure*". It is achieved in a well-defined section of the conduit, generally at the outlet. In this section, the flow rate is equal to the speed of sound in the fluid, so much so that disturbances generated downstream do not affect the upstream flow.

Experience shows a similar phenomenon for two-phase flows. On the other hand, it is more difficult to determine the value of the pressure wave propagation rate in a two-phase fluid given that these waves do not move at the same speed in each of the two phases. However, the experiments conducted for the two-phase flow study demonstrated that the speed of sound of a two-phase flow is markedly lower than the speed of sound of a single-phase flow (Delhaye, 1981). As a result, the critical flow is achieved more easily in the case of a two-phase flow (May, 1996).

The modelling of the flow rate at the opening using the method proposed by Wheatley (April 1997) assumes that the two-phase flow is critical which is equivalent to considering that the velocity of the fluid at the outlet, U_b, is equal to the speed of sound in the two-phase fluid of quality x_b.

Due to the flow isentropy hypothesis, the speed of sound can be obtained using the equation:

$$U_{sound} = \sqrt{\left.\frac{\partial P}{\partial \rho}\right|_{S=ct}} \quad (7)$$

In the case of a two-phase fluid, integration at constant entropy is relatively complex. Finally, it was demonstrated that the speed of sound is expressed as follows:

$$U_{sound} = \frac{P_b.A_0}{\rho_b.T_b\sqrt{Cp_{liq}.T_b\left(1+\left(\frac{A_0}{T_b}+1\right).Ln\left(\frac{T_{int}}{T_b}\right)\right)}} \quad (8)$$

The density of the fluid at the opening, ρ_b, is obtained using the flowing equation:

$$\frac{1}{\rho_b} = \frac{1}{\rho_{liq}} + \frac{Ln\left(\frac{T_{int}}{T_b}\right)Cp_{liq}.T_b{}^2}{A_0.P_b} \quad (9)$$

In this case, the pressure P_b such that $U_b = U_{sound}$ (equations 6 and 8) is sought using an iterative process. Once this pressure is obtained, the release temperature is known (saturation) and the quality at the opening is determined using equation 4:

$$x_b = \frac{\frac{1}{\rho_b} + \frac{1}{\rho_{liq}}}{\frac{1}{\rho_{gas}} + \frac{1}{\rho_{liq}}} \quad (10)$$

The mass flow rate, G_b, is then determined using the conventional equations:

$$G_b = \rho_b.A_b.U_b \quad (11)$$

where A_b is the opening surface area

The release pressure value found by testing the equality between the release velocity and the speed of sound will determine the type of release. In fact, if this value is above atmospheric pressure, the flow will be critical and the jet will accelerate further after the opening due to its expansion to atmospheric pressure.

On the other hand, if the pressure obtained is below atmospheric pressure, it has no physical significance. In this case, the flow will not be critical (the fluid at the opening does not reach the speed of sound) and the pressure at the opening is considered to be equal to the atmospheric pressure.

Non-equilibrium models

Models closer to reality exist, referred to as "non-equilibrium models". They make it possible to account for thermodynamic differences existing with liquid-vapour equilibrium.

In addition, they include the fact that the two phases are separate, and are considered separately, i.e. that they can have different velocities and that phase changes may be limited by heat transfers or accelerated by the presence of irregularities.

An example includes the "frozen" model which makes the simple assumption that there is no change of phase. The flow is then modelled using Bernoulli's equation.

The actual separate phase model evaluates the material, energy and quantity of movement on each of the two phases and applies a vaporisation law in view of the flow state. This model is based on empirical correlations qualifying the flow states.

More comprehensive models such as Yan's model (1991), which models nucleation, also exist. It particularly makes it possible to estimate the frequency of occurrence of bubbles and the progression of their size.

In order to compare the experimental values to theoretical values, two models (Fauske and Wheatley) were used on the basis of the test conditions for the tests conducted by INERIS and described in chapter 4 above. As a general rule, the results obtained using these models differ substantially from the values recorded during the tests, where the values obtained using the models were generally greater than the experimental values.

These results confirm the fact that the modelling of the flow rate in the case of a two-phase flow is highly complex and that simplified models are unable to account for all the phenomena arising during flow. In addition, within the scope of these tests, which were not intended to study the flow rate at the opening in an in-depth way, but simply to determine it, the release system used consisted of significant pressure drops on a pipe over 12 metres in length.

We verified experimentally that the fluid at the orifice was indeed under saturation conditions, i.e. that the (T_b,P_b) pairs measured experimentally corresponded to the (T_b,$P_{sat}(T_b)$) pairs, the basic hypothesis for HEM models.

In conclusion, these models are suitable for tank leakages or releases after a short pipe. They do not account for pressure drops and, therefore, ammonia vaporisation during its transport outside. If an opening is considered to be flush with the tank wall, ammonia is vaporised instantaneously into the atmosphere without passing via the three flow states (bubble state, annular state and dispersed flow).

In the tests conducted, the pipe is sufficiently large for the flow to pass via these three flow states. In the literature, it is admitted that dispersed flow is established when the condition L>2D is met (L pipe length, D pipe diameter), which is the case. In this way, the dynamic behaviour of ammonia is influenced by these three states and the phenomena are complex to model.

5.2 WEATHER CONDITIONS DURING THE TESTS

The weather conditions are described using a number of parameters, the main one being associated with the wind velocity, on one hand, and atmospheric turbulence, on the other.

For each test, the atmospheric conditions were recorded using the equipment described in chapter 4 above. During the recording period, some values measured were subject to little and slow variation. This particularly applied to the ambient temperature, relative humidity and solar flux. Note that these values were measured on the weather station next to the control station.

However, other values, such as the wind velocity and direction measured on the weather mast referenced M in figure 11, could be very variable during the recording period.

In order to give an order of magnitude of the weather conditions during the tests, the mean values associated with each of the releases are given in the table below.

Test No.	Mean atmospheric conditions				
	Sheltered temperature	Relative humidity	Solar flux (kW/m^2)	Wind velocity at height of 7 m	Wind direction at height of 7 m
1	14℃	76%	0.2	5 m/s	260°
2	8.5℃	84%	0.1	3 m/s	305°
3	5℃	90%	0.04	2.5 m/s	5°
4p	10℃	61%	0.5	3 m/s	10°
4	12.5℃	82%	0.25	3 m/s	290°
5	20℃	50%	0.65	3.5 m/s	310°
6	12℃	75%	0.5	5 m/s	285°

7	13°C	60%	0.7	6 m/s	310°
8	20°C	37%	0.7	5 m/s	275°
9	14°C	50%	1.0	3 m/s	355°
10	24°C	20%	1.0	3 m/s	10°
11	24°C	24%	0.7	5 m/s	310°
12	15°C	33%	0.6	6 m/s	310°
2b	18°C	31%	0.7	4 m/s	315°
8b	18°C	31%	0.6	5 m/s	310°

table 18: mean atmospheric conditions during each release

In addition, to evaluate the dispersion of ammonia in the atmosphere, it is important to characterise the atmospheric turbulence well.

The atmospheric turbulence is due both to turbulences of mechanical origin, generated by ground roughness, and turbulences of thermal origin associated with the vertical stratification of the temperature of the atmosphere. It can be evaluated by recording wind velocity and direction fluctuations at one point.

A distinction can be made between two types of turbulences of mechanical origin: small-scale turbulence and large-scale turbulence.

Small-scale turbulence, generated by the friction of wind on the ground, is influenced by roughness. It is applied within a layer of some hundred metres in height. This type of turbulence is a predominant factor in the dispersion phenomenon.

Large-scale turbulence is associated with distant weather phenomena. It influences the transport or diffusion of particles, if the study site covers several dozen kilometres, which is not the case in this programme.

In the case of turbulences of thermal origin, an important characteristic is the atmospheric stability. It is associated with the vertical air density gradient, in turn associated with the vertical temperature gradient. The adiabatic vertical temperature variation is between -0.6°C/100 m and -1°C/100 m according to the air humidity level. To simplify, when the vertical temperature gradient is below that of an adiabatic atmosphere, the atmosphere is said to be unstable. If the gradient corresponds to the adiabatic, the atmosphere is said to be neutral. Finally, if the thermal gradient is positive (therefore, greater than that of the adiabatic), the atmosphere is said to be stable, in other words, unfavourable to effective vertical diffusion of a pollutant.

With this respect, Pasquill proposes a classification comprising 6 stability classes, referenced A to F, covering cases of very unstable to unstable atmospheres (classes A and B) to cases of stable to very stable atmospheres (classes E and F), including neutral cases (classes C and D).

If an atmosphere is unstable (Pasquill's classes A and B), atmospheric dispersion is favoured, resulting in the formation of a very open plume (see figure 13, Pasquill, 1974).

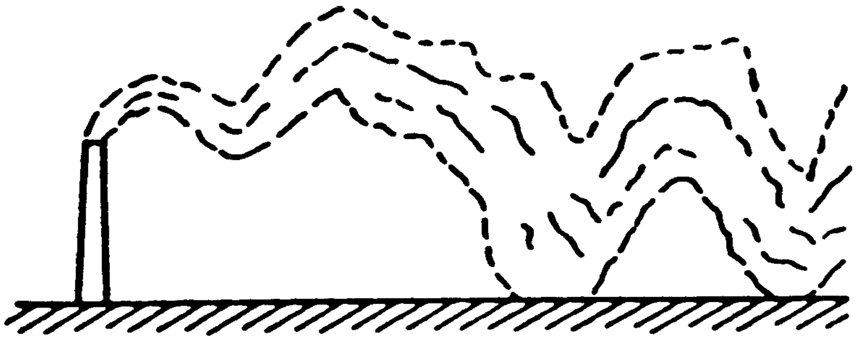


figure 13: Dispersion in an unstable atmosphere (taken from Pasquill, 1974

On the other hand, if an atmosphere is stable, its ability to diffuse a pollutant vertically is low, resulting in the formation of a very closed plume (see figure 14, Pasquill, 1974).

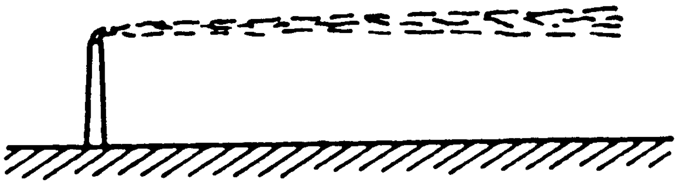


figure 14: *Dispersion in a stable atmosphere* (taken from Pasquill, 1974

From an experimental point of view, there are different methods available to determine the stability of the atmosphere, such as, for example, the determination:

- of the standard deviation of the wind direction (σ_θ) ;
- of the vertical temperature gradient (ΔT) ;
- of the Richardson number (Ri) ;
- of the Monin-Obukhov length ;

- or, methods based on criteria such as the mean wind velocity at a fixed height, the altitude of the sun, cloud coverage, etc.

On the basis of the different values measured during the test campaign, we applied two of these methods: the determination of the standard deviation of the wind direction (σ_θ) and the method based on the determination of the Monin-Obukhov length. After a brief description of these methods, we will present the results obtained for all the tests.

Standard deviation of the wind direction (σ_θ)

The standard deviations of the wind direction essentially represent the horizontal stability of the atmosphere (the vertical turbulence of the atmosphere being estimated on the basis of the vertical temperature gradient).

For each test, the standard deviation of the wind direction (σ_θ) was calculated over a period comprising approximately 5 minutes before the test, the duration of the test and approximately 15 minutes after the test, i.e. a period of approximately one half-hour.

Determination of Monin-Obhuckov length

For each of the tests, we also determined the Monin-Obukhov length which is a characteristic length of atmospheric turbulence. This length, referenced L, is defined as follows:

$$L = -\rho C_p u^* k (g/T_0) H$$

where ρ is the density of the fluid, C_p is its heat capacity, u^* is the friction velocity, k in the von Karman constant, g is the gravity constant, T_0 is the temperature at ground level and H is the vertical heat flux.

The values of u^* and H were determined using the values measured by the ultrasonic anemometer with an acquisition frequency of 10 Hz.

Golder (1972) defined a relationship between Pasquill's stability classes, the mean site roughness z_0, and the length L.

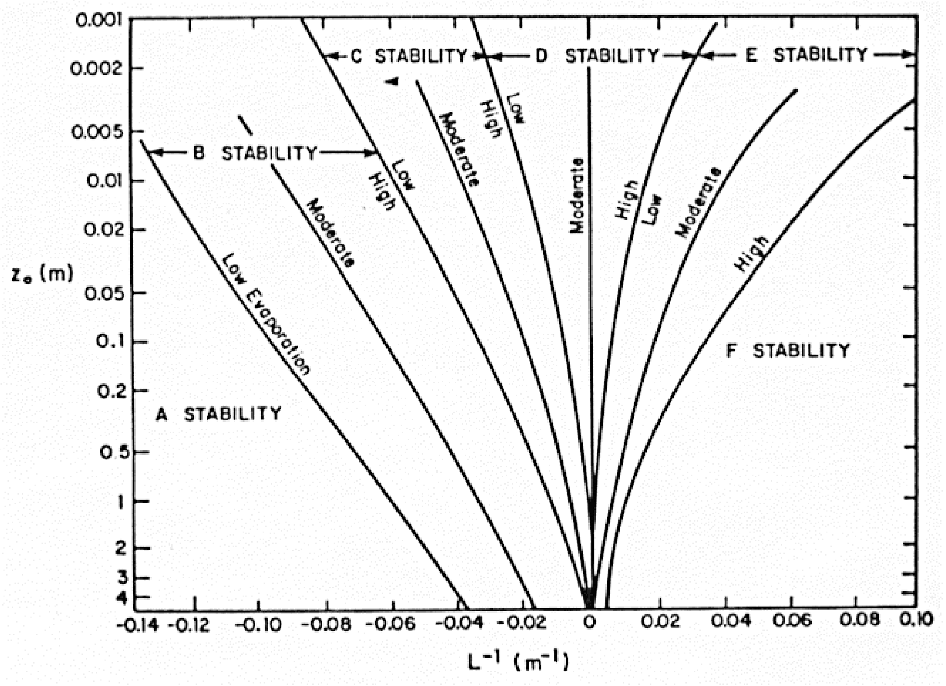


figure 15: Relationship between the Monin-Obukhov L and the roughness z_0 for different Pasquill stability classes (Golder, 1972).

On the basis of the values recorded during the tests, the values of σ_θ and L were calculated. Then, for each test, the Pasquill stability classes were estimated using each of these two methods. The results obtained are given in the table below. In addition, for each of the tests, an estimation of the visible plume length is given.

Test No.	Estimated atmospheric stability classes		estimation of visible plume length (m)
	by determining the standard deviations of the wind direction (σ_θ)	by determining the Monin-Obukhov length (L)	
1	D	-	≈ 5 m
2	D	C/D	≈ 500 m
3	C	D	≈ 350 m
4 prel.	C	-	≈ 400 m
4	C	D	≈ 500 m
5	A	B	≈ 30 m
6	D	D	≈ 60 m
7	C	C/D	≈ 60 m
8	D	C	≈ 25 m
9	A	B/C	≈ 120 m then ≈ 30 m
10	A	A/B	≈ 70 m
11	C	C	≈ 70 m
12	D	C/D	≈ 70 m
2b	A	A/B	≈ 60 m
8b	C	B/C	≈ 15 m

-: not determined

table 19: Atmospheric stability classes estimated during tests

The use of these methods, for given atmospheric conditions, may result in different stability classes. However, during the tests, no significant differences were observed.

In addition, in relation to the general atmospheric conditions during the tests, the following points were noted:

- From test No. 4, there was no rain on the test site. In this way, relatively low daytime relative humidity levels were observed (up to 20% for test No. 10) ;
- The visible part of the plume varies considerably. As mentioned above, this is essentially due to the relative humidity level of the atmosphere. In fact, the ammonia cloud is relatively cold (approximately -40℃ on the release axis 20 metres from the release point) due to the presence of ammonia droplets which take up the heat, particularly in the ambient air, to vaporise. The low temperatures reached mean that the water vapour present on the plume path is condensed and forms a visible cloud until the plume is heated by diluting with ambient air.
  In this way, for almost identical release conditions (tests 4 and 11), the visible part of the plume changed from approximately 500 metres to approximately 70 metres for a relative humidity level which changed from 82 to 24% ;
- The solar flux varied considerably between the tests, with very low values at the start of the campaign (0.04 kW/m^2) and high values in April (1 kW/m^2) ;
- For all the tests, the mean wind velocity oscillated between 2 and 6 m/s. The mean wind direction for each test was very variable. These mean wind directions for each test are given in figure 16 overleaf.

photo 3: Typical ammonia plume

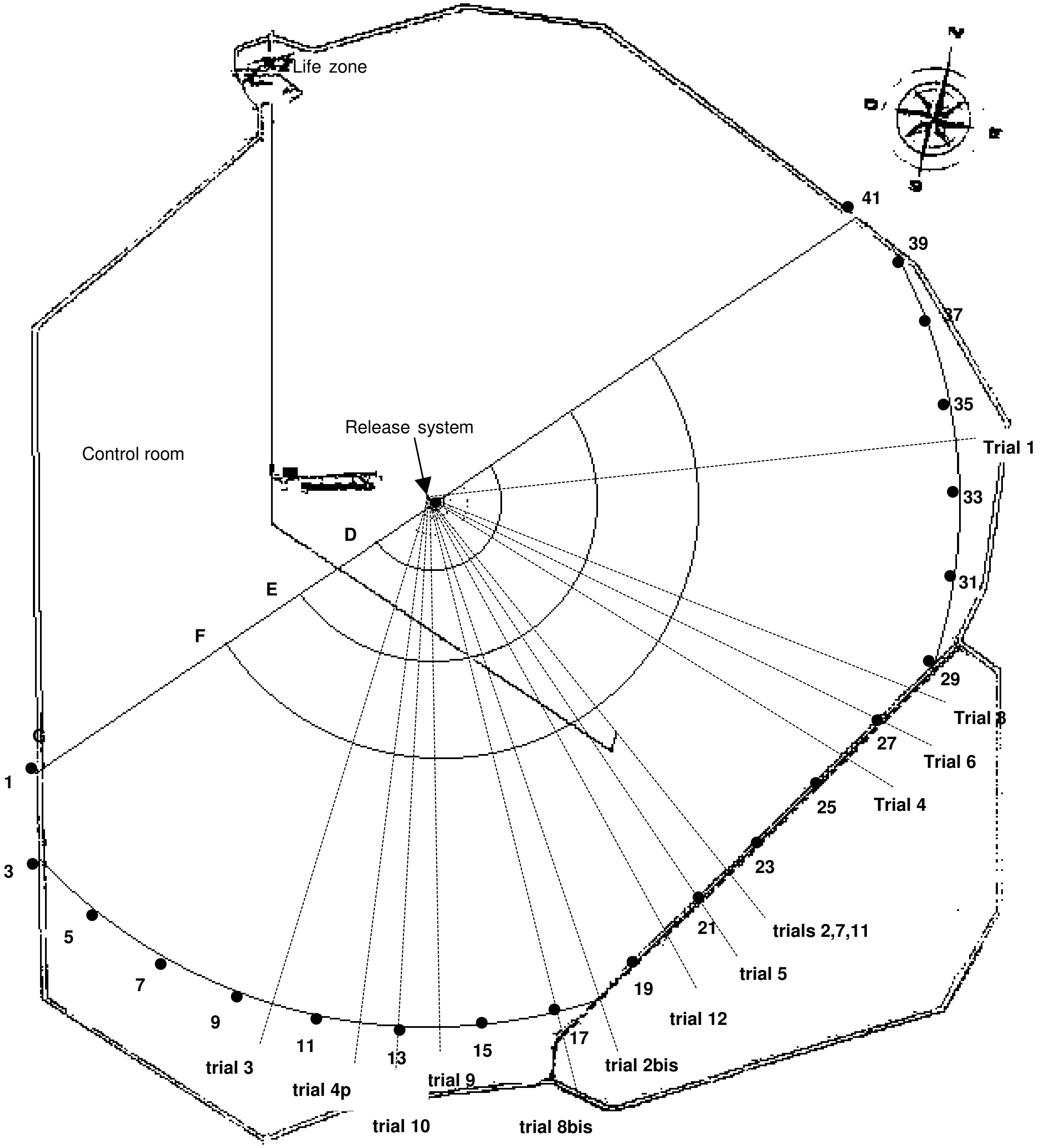


figure 16: mean wind direction for each test

6. MEASUREMENTS RECORDED LEEWARD FROM RELEASES

The values recorded by the ammonia concentration sensors leeward from the releases are given in the sub-section below.

These values are then analysed in sub-section 6.2.

6.1 AMMONIA CONCENTRATION SENSORS

Note that the ammonia concentration measurement equipment used in the test campaign is described in chapter 4. These concentrations were essentially measured leeward from the releases on 7 arcs.

The responses from the concentration sensors were very different according to their positions with reference to the plume axis and with reference to the distance from the release point.

For example, the two figures below give two signals representing the ammonia concentrations (in ppm) recorded during test No. 2 leeward from the release, by a pellistor located 100 metres from the release point (figure 17) and by an electrochemical cells located at a distance of 800 metres (figure 18). Note that the release time was 440 seconds.

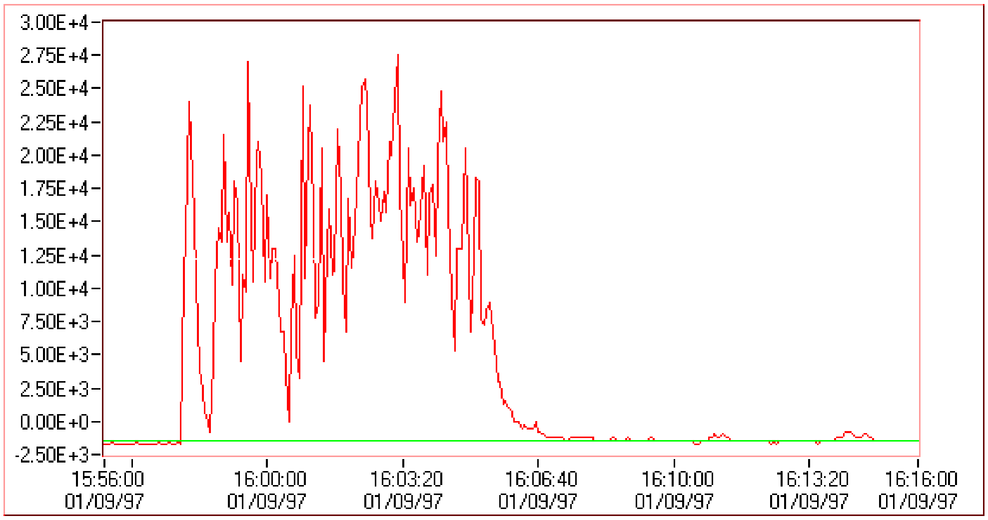


figure 17: Progression over time of ammonia concentration (in ppm) 100 m from release point observed during test 2.

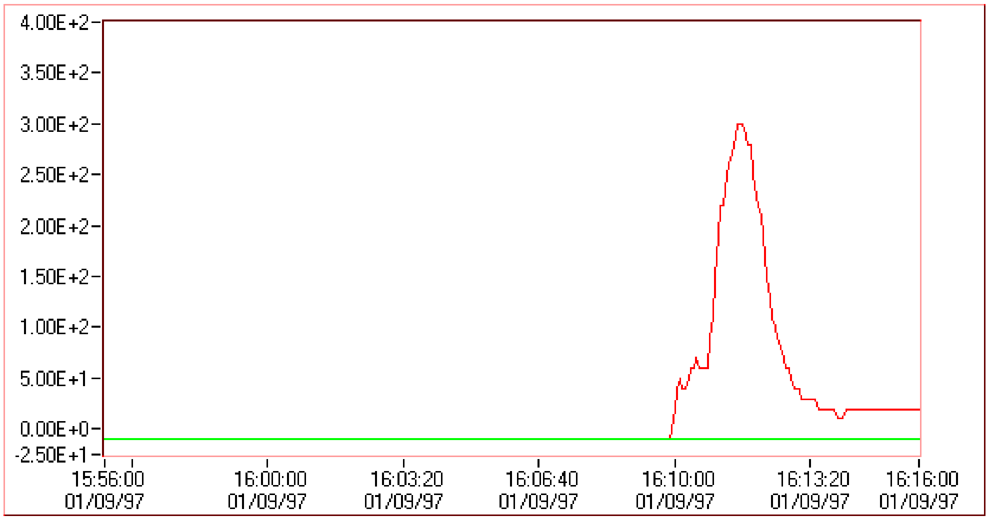


figure 18: Progression over time of ammonia concentration (in ppm) 800 m from release point observed during test 2.

Depending on the phenomena under study, there are different options for the analysis of the fluctuations in concentration recorded during the tests. In this document, the concentration values given are mean values of the concentrations measured on the plume axis.

To obtain these values, we recorded, at each time interval (4 s), the maximum concentration value on each of the 6 arcs located 20, 50, 100, 200, 500 and 800 metres from the release point. Then, on each arc, we calculated the mean of all the maximum values recorded over time, excluding the first and last minute of exposure of each sensor. The start of sensor exposure was determined by accounting for a cloud advection time. This time was taken to be equal to the ratio of the distance between the arc in question and the release point over the mean wind velocity during the release.

The table below gives the mean concentration values determined in this way on the plume axis for each of the tests conducted.

	mean concentrations in ppm **measured at height of 1 m on release axis**					
Test No.	**20m**	**50m**	**100m**	**200m**	**500m**	**800m**
1	15000	4500	1500	400	40	10
2	55000	31000	20000	9000	900	300
2b	33000	18000	6600	1600	60	20
3	33000	20000	800	2700	250	100
4	65000	27000	16000	10000	1200	500
5	28000	14000	6500	1500	140	30
6	28000	13000	7300	2500	450	150
7	25000	11000	5300	1000	160	60
8	26000	12000	-	-	-	-
8b	20000	8500	4000	800	70	30
9	20000	5000	2000	450	30	5
10	65000	29000	18000	4000	80	20
11	65000	27000	15000	3500	300	80
12	60000	20000	7000	1500	120	-

-: concentration value on plume axis not measured

table 20: Mean ammonia concentrations on plume axis at height of 1 m

Test 4p described in chapter 4 was an intermediate test to validate the procedure for the subsequent tests. The concentration values measured during this test did not make it possible to determine the mean values leeward from the release. Therefore, this test is not mentioned in the above table.

The ammonia concentration values given in table 20 above were rounded off in view of the precision of the sensors. The progression of the ammonia concentrations on the plume axis as a function of the distance to the release point was plotted for each test. These progressions are given in figure 19 overleaf.

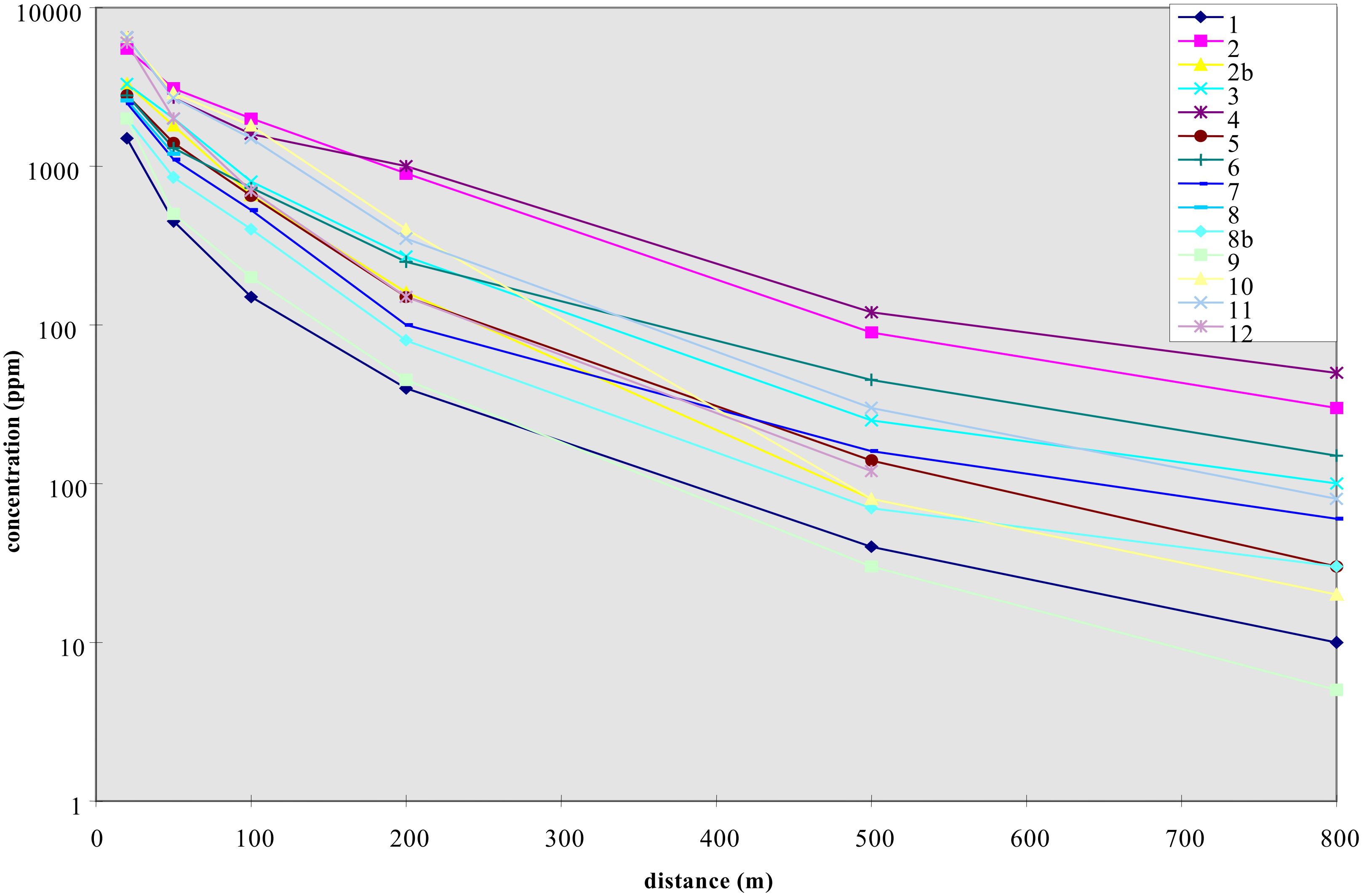
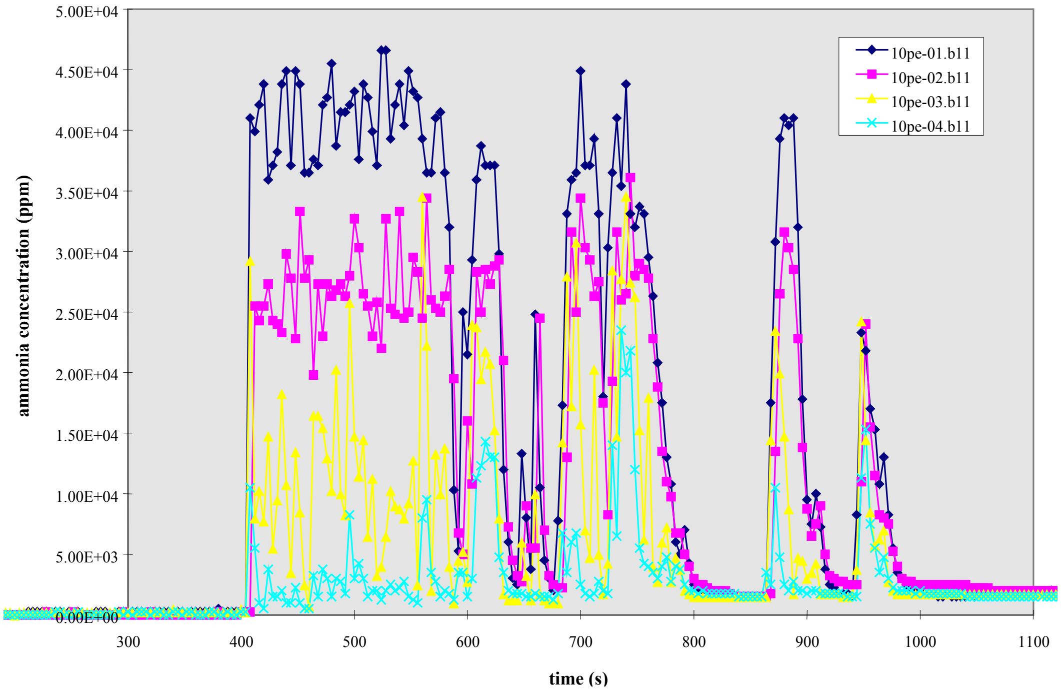


figure 19: Progression of ammonia concentrations on plume axis as a function of distance to release point

As a general rule, after the tests, several remarks can be noted:

- Liquefied ammonia releases behave like heavy gas releases as illustrated in figure 20 below. In this figure, we have indicated the response of 4 sensors located on the same mast 50 metres from the release point and on the plume path axis during test 10.



Legend '10pe-01.b11': The first number '10' corresponds to the trial number, the two letters 'pe' (or 'tc' or 'ec') corresponds respectively to the sensor type (pellistor, thermocouple or electrochemical cell), the number '01' corresponds to the height level, and the extension corresponds to the mast number.

figure 20: Progression of ammonia concentration values for sensors located on the same mast 50 metres from the release point.

On this mast, the sensor heights, referenced 01 to 04 in the legend associated with these curves, are 0.1 m, 1 m, 2 m and 3 m above ground level, respectively.

The vertical ammonia concentration gradient is high 50 metres from the release point. In fact, at ground level, the concentration is greater than 40,000 ppm (4%) and is more than 10 times lower at a height of 3 m for this test.

In addition, since the weather conditions were unstable on the day of this test, considerable fluctuations in the ammonia concentration values are observed at times.

The vertical ammonia concentration gradient is still pronounced 100 metres from the release point, as illustrated in figure 21 below for two sensors at heights of 1 and 3 metres.

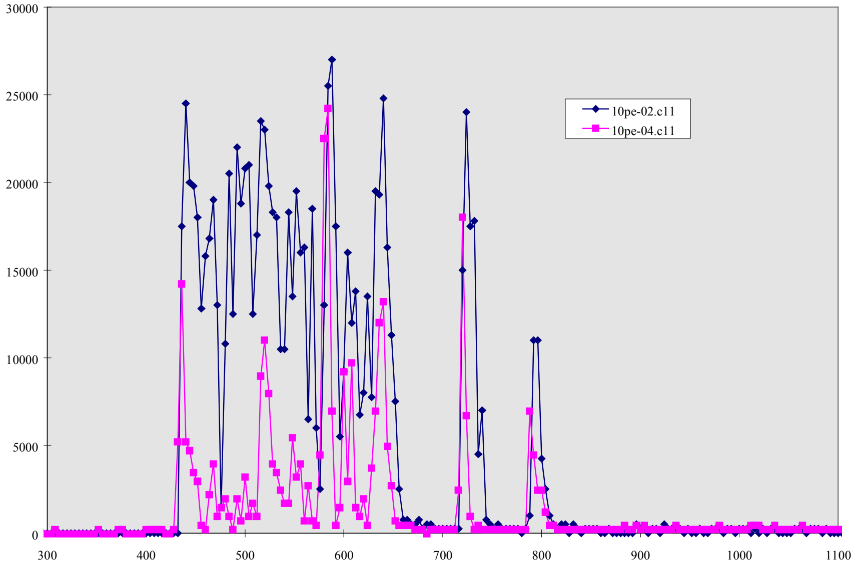


figure 21: Progression of ammonia concentration values for sensors located on the same mast 100 metres from the release point

As a general rule, a vertical concentration gradient within the cloud was still observed 200 metres from the release point.

That being said, from 500 metres, the concentration values measured at heights of 1 and 3 metres above ground level were practically identical as illustrated in figure 22 below.

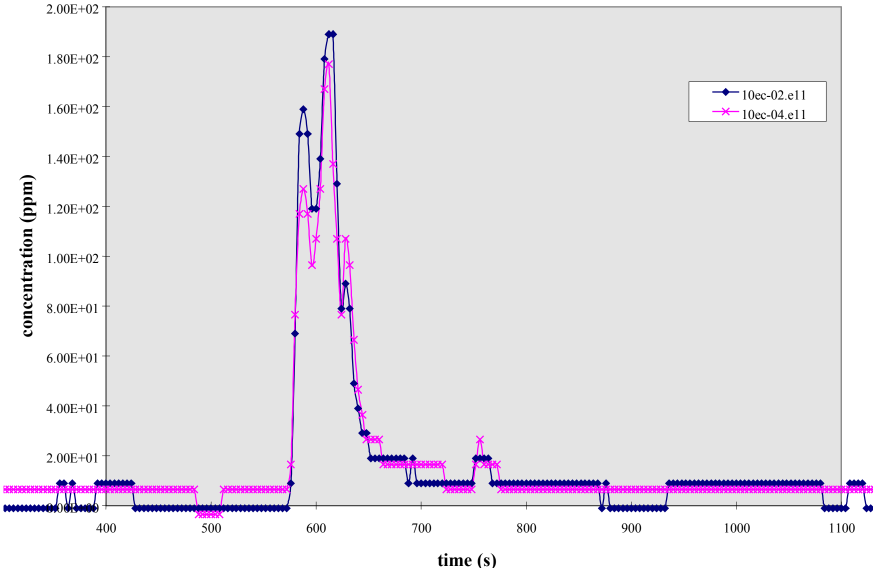


figure 22: Progression of ammonia concentration values for sensors located on the same mast 500 metres from the release point

- For the gaseous phase ammonia release, heavy gas type behaviour was also observed on the sensors located 20 metres from the release point (see figure 23). However, 50 metres from the release point, this effect is practically not noticeable.

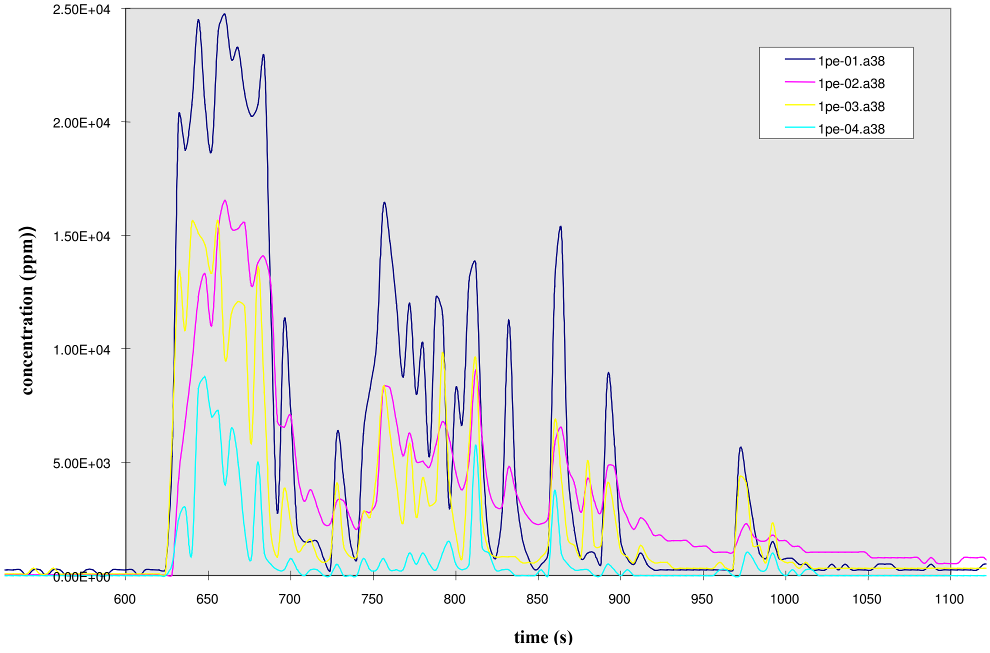


figure 23: Progression of ammonia concentration values 20 metres from the release point

In addition, throughout the tests, no rise in the ammonia cloud formed was observed.

6.2 ANALYSES

In this section, we will study the influence of some parameters on the atmospheric dispersion of ammonia. These parameters are as follows:

- the type of orifice ;
- the atmospheric stability ;
- the presence of obstacles ;
- the presence of a retention dike ;
- and the use of peacock tails.

Finally, in the final section, the experimental results measured during this test campaign are compared to calculation results obtained using an integral atmospheric dispersion software program.

6.2.1 Influence of release orifice

During the tests, 4 types of orifice were used on the release system, i.e.:

A) a 18 mm diameter orifice	Test 2b
B) a 20 mm diameter orifice	Test 2
C) a 2 inch flange (50.8 mm)	Test 3
D) and a 50.8 mm diameter orifice	Tests 1, 4, 10, 11, 12 (5 open-field releases)
	Tests 5, 6, 7, 8, 8b, 9 (6 impacting releases)

These 4 types of orifice will be referenced A to D hereafter.

In order to evaluate the influence of the type of orifice on atmospheric dispersion, an ammonia plume width was estimated for the 8 open-field releases at the arc located 20 metres from the release point. To estimate this width, for each test, we determined the zone in which the ammonia concentration was greater than or equal to half the maximum concentration recorded at 20 metres. The results obtained are given in the table below.

orifice type	**test**	**plume width where C > Cmax/2**	**associated angular sector**
A	2b (diam. 18 mm)	9 m	25°
B	2 (diam. 20 mm)	9 m	25°
C	3 (flange)	49 m	140°
D	1	4 m	11°
	4	5 m	15°
	10	6 m	18°
	11	5 m	16°
	12	7 m	20°

table 21: plume width for open-field releases

Several remarks can be made on the basis of this table:

- The release via the flange (orifice C) produces, in the near field, the widest cloud of all the open-field tests. This is essentially due to the fact that the nozzle orients the ammonia projection along directions perpendicular to the release axis. The resulting plume is extended in width, progressing axially with the wind. In this way, despite a 33% greater flow rate than test 2b, the ammonia concentration values measured during test 3 with the flange are of the same order of magnitude as for test 2b over the first 50 metres;

- The tests in which the end if free (50.8 mm diameter orifice D) result in jets referred to as "linear jets". Under these conditions, the width of the plume is narrower than under other conditions;

- Finally, the releases in which a diameter restriction was added at the end (orifices A and B) result in greater plume widths. This may be due to the fact that, for these tests, restricting the diameter at the orifice results in a pipe pressure at the opening (> 5 bar) which is greater than the pressure at the opening for tests with no diameter restriction (between 1.5 and 3 bar). As a result, the thermodynamic flash that takes place at the outlet into the atmosphere is more significant and, therefore, the resulting volumetric expansion results in a larger plume size.

In sum, the orifices affect the physiognomy of the cloud (width, height) and, as a result, the mean concentrations. This is clearly visible and measurable during the first 50 metres. At greater distances, this influence wears off in favour of that of the atmospheric stability, as demonstrated below in this report.

6.2.2 Influence of atmospheric stability

The influence of the release conditions in the near field may be considerable over a few dozen metres after the release point. At further distances, the atmospheric stability becomes predominant as the passive dispersion phase is then involved.

In this way, significant differences in concentrations may be observed in the far field for releases with identical flow rates but with different atmospheric stability conditions. For example, tests 5 and 6 were conducted with similar release conditions and with different atmospheric conditions, type (A/B; 3.5 m/s) for test 5 and type (D; 5 m/s) for test 6, respectively.

In addition, tests 10 and 11 were conducted on the same day, the first in the early afternoon and the second in the late afternoon, with identical release conditions and different atmospheric conditions, type (A/B; 3 m/s) for test 10 and type (C; 5 m/s) for test 11, respectively.

The progressions of the concentrations in tests 5 and 6, on one hand, and tests 10 and 11, on the other, are described in the graph in figure 24 below

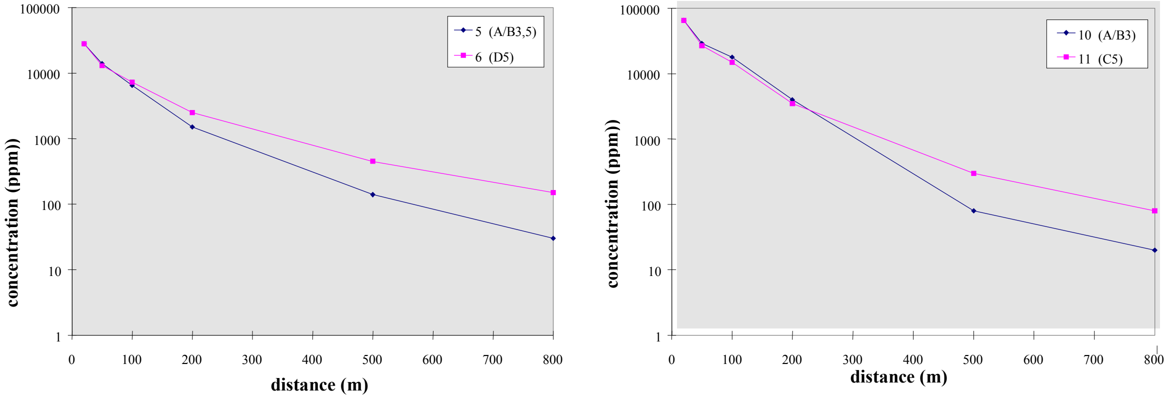


figure 24: Progression of concentrations on release axis as a function of distance for different weather conditions.

In these graphs, a difference in concentration of a factor of 4 to 5 can be observed 800 metres from the release point while the concentrations are practically equal in the first 100 metres.

In addition, tests with the same type of atmospheric conditions were conducted during the test campaign. When these tests are compared to each other, a similar plume dilution is observed for all the tests. For example, in the figure below, we have reproduced two graphs showing the dispersion conditions of tests 2 and 4, in which the release conditions were similar (similar flow rate, different cross-sections) and tests 8b and 11, in which the release conditions were different.

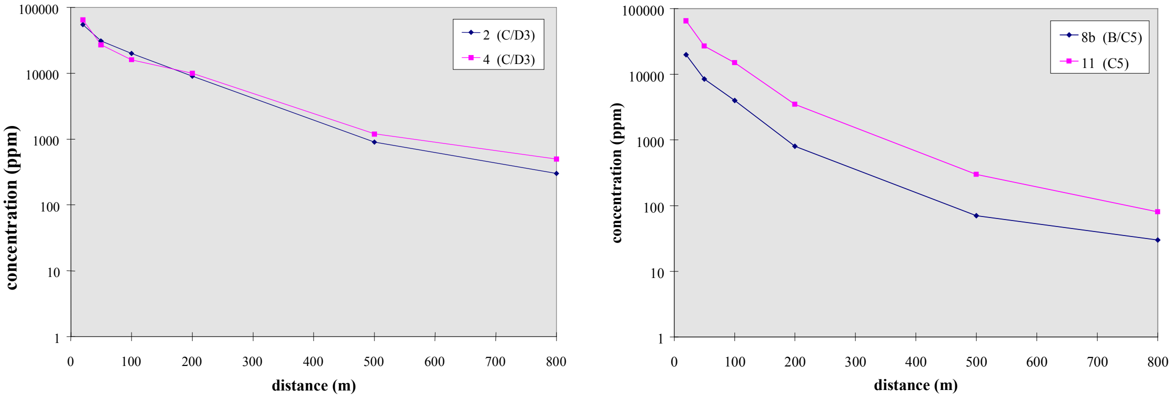


figure 25: Progression of concentrations on release axis as a function of distance for similar weather conditions.

The progression of the ammonia concentrations as a function of the distance to the release point is almost identical for the tests. It is important to note that, in reality, the atmospheric flow is difficult to reproduce, and, as such, it is unlikely that two tests with the same source term would give identical results in terms of concentrations leeward from a release.

6.2.3 Influence of obstacle placed in near field

During the test campaign, six releases impacting a surface in the near field were used, i.e. tests 5, 6, 7, 8, 8b and 9. Note that tests 5 and 6 were horizontal releases against a wall positioned 3 metres and 1 metre from the release point, respectively. The 4 other tests related to vertical releases falling and impacting the ground. For tests 7 and 8, there was no retention dike on the ground. For tests 8b and 9, a retention dike was installed. The last two tests will be studied in the section below entitled "Influence of retention dike".

Note that, during tests 5 to 9, the atmospheric stability conditions determined experimentally were practically all different, ranging from class A/B to class D.

In the case of the two horizontal releases impacting a wall, the release conditions are similar to the conditions for test 4 (open-field release). Therefore, a comparison of these three tests was conducted. The progression of the ammonia concentration values leeward from the release is given in the figure below for these three tests.

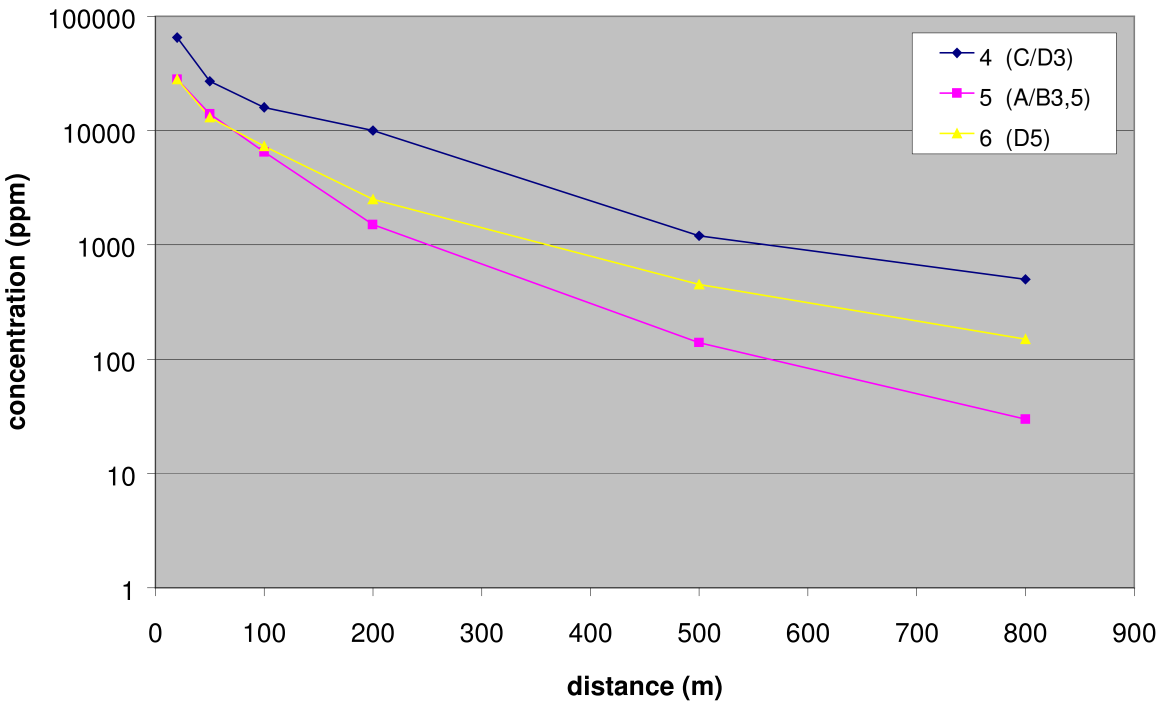


figure 26: Progression of concentrations as a function of distance for tests 4, 5 and 6

It is noted that the ammonia concentration values recorded for tests 5 and 6 after the wall 20 and 50 metres from the release point are very similar, whether the wall is located 1 or 3 metres from the release point.

However, when the release is produced in an open field, the ammonia concentration values recorded by the sensors are greater by a factor of 2 up to 50 metres from the release point. After that, it is more difficult to compare the values, since the influence of the weather conditions is predominant on the dispersion of the plume.

Two phenomena can explain the decrease in the concentration in the near field (less than 50 metres from the release site in this case) in the changeover from test 4 to tests 5 and 6.

Firstly, there was an increase in the level of mechanical turbulence, because the plume is obliged to deviate the obstacle formed by the wall. In this case, the air flows via the sides and the top of the wall.

Secondly, the impact of the ammonia jet consisting of fine droplets on the front of the wall results in the formation of a very cold liquid ammonia film which favours the trickling of the droplets and the formation of a pool at the base of the wall. With this respect, the thermocouples installed on the release slab for tests 5 and 6 give:

- temperature values between -40℃ and -60℃ for the thermocouples installed on the wall ;
- and temperature values of the order of -60℃ throughout the release for the majority of those installed at ground level.

In this way, one of the effects of the presence of a wall in the near field of a liquefied gas release is to favour the recondensation of part of the ammonia released and, through the formation of a liquid ammonia film, induce the trickling of the liquid phase. This immediately results in a decrease in the ammonia concentrations downstream from the wall. It is important to note that, for these two tests, there was no retention dike. In this way, part of the liquid ammonia was dispersed over a surface area, the size of which is difficult to estimate. This liquid ammonia was then vaporised. From this point of view, no calculations were made.

In section 6.1, we saw that the ammonia cloud behaved like a heavy gas up to a distance of more 200 metres from the release point when it was released in liquid phase under our test conditions, particularly in the form of an open-field jet. On analysing the results, it has emerged that this heavy gas type behaviour is less pronounced for releases impacting a wall in the near field.

Typically, when the release was carried out in an open field, two sensors installed at two different heights, on the same measurement mast located 50 m from the release point, give concentration values at a height of 3 m that are 5 to 10 times lower than those measured at a height of 1 m.

After an impact against a wall, the vertical concentration gradient is such that the concentration values measured at a height of 3 m are only approximately two times lower than those measured at a height of 1 m.

- In the case of the two vertical releases impacting the ground with no retention dike (tests 7 and 8), their release conditions were similar to those for tests 4, 5 and 6. The graph below shows the progression of the ammonia concentrations leeward from the releases for tests 4, 5, 6, 7 and 8.

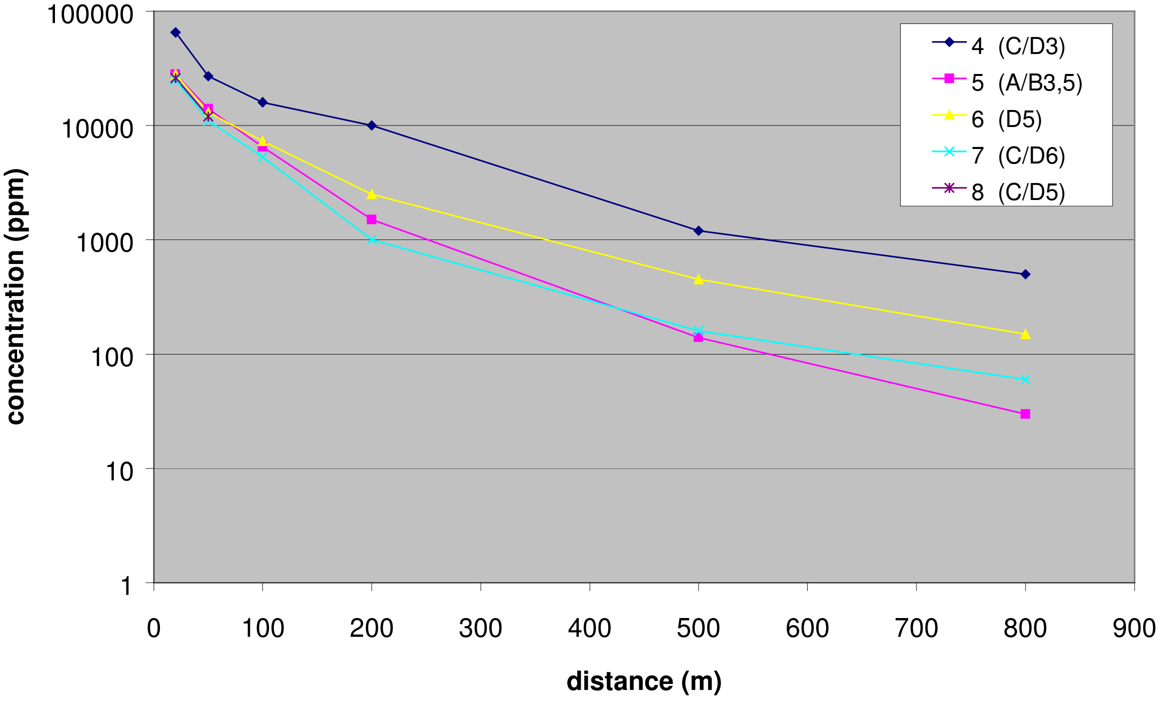


figure 27: Progression of concentrations as a function of distance for tests 4, 5, 6, 7 and 8.

In the above figure, test 8 is not shown after 50 m due to a change in the wind direction during the test such that the measurements made could not indicate the mean concentration on the shifted cloud axis. However, the ammonia concentration level appears to be of the same order of magnitude up to 50 m from the release point for the four tests in which an obstacle was encountered.

The release conditions for tests 7 and 8 are such that the mass flow rate for these tests (3.9 kg/s) is slightly lower with reference to tests 4, 5 and 6 (4.2 kg/s). As for tests 5 and 6, roughly the same difference in concentration is found between tests 7 and 8 and test 4, i.e. a decrease of approximately 50% up to 50 m from the release point. Beyond this point, we do not have sufficient information to be able to compare with test 8.

The release conditions for tests 7 and 8 are such that the mass flow rate for these tests (3.9 kg/s) is slightly lower with reference to tests 4, 5 and 6 (4.2 kg/s). As for tests 5 and 6, roughly the same difference in concentration is found between tests 7 and 8 and test 4, i.e. a decrease of approximately 50% up to 50 m from the release point. Beyond this point, we do not have sufficient information to be able to compare with test 8.

In the case of tests 4, 6 and 7, the stability of the atmosphere was still considered as neutral (Pasquill classes C or D). However, the wind velocity is different for these three tests. The mean velocity during these three tests was calculated between 3 and 6 m/s, with velocity ranges between 1 and 10 m/s. The difference in the progression of the ammonia concentrations leeward from releases 6 and 7 can be explained in two ways:

- by improved plume dilution due to more favourable atmospheric conditions;
- by a larger quantity of liquid ammonia trapped around the release point.

In addition, temperatures of the order of -60°C were recorded on the ground for each test. It was not possible to obtain an accurate estimation of the size of this pool and even less so of its thickness (thin in principle). During the release, the pool was evaporated. Once the release had been completed, some sensors still detected temperatures below -50°C 4 minutes after the end of the release, which underlines the size of the pool on the ground, without having the possibility to quantify it in the absence of a retention dike.

In sum, orienting a release against a wall or against the ground appears to induce a significant reduction in ammonia concentrations leeward from the release (approximately 50% in our release configurations) in both the near field and the far field.

6.2.4 Influence of retention dike

Of the fifteen tests conducted during this campaign, a retention dike was set up on the release slab for tests 8b and 9. The release configuration is identical for these two tests, i.e. the vertical releases impacting the ground from a height of 1 m. Only the size of the retention dike is different in these two tests. For test 8b, the surface area of the retention dike was 100 m^2 and the height 5 cm, i.e. a retention volume of 5 m^3. For test 9, the surface area of the retention dike was reduced to 4 m^2 and the height was 1 m, i.e. a retention volume of 4 m^3.

In the previous section relating to releases impacting an obstacle (tests 5, 6, 7 and 8), we saw that, as a general rule, at the end of each impacting release, the concrete slab was extensively wetted with liquid ammonia. In particular, for releases directly impacting the ground, the entire slab was wetted. However, the quantity of liquid ammonia on the ground was not estimated. However, tests 8b and 9 can be used to estimate the quantity of liquid ammonia trapped on the ground.

In test 8b, 2120 kg of ammonia was released throughout the test. At the end of this test, a height of approximately 1.5 to 2 cm of liquid ammonia could be observed in the retention dike, i.e. a volume of approximately 1.5 to 2 m^3. The temperature of the liquid ammonia at the end of the release was approximately -60°C as for the previous tests. In this way, it is possible to estimate that the quantity of liquid ammonia present on the release slab was between 1050 and 1400 kg, which represents between 50% and 65% of the total mass quantity released.

In test 9, 2370 kg of ammonia was released throughout the test. At the end of test 9, a height of approximately 55 cm of liquid could be observed in the retention dike, i.e. a volume of approximately 2.2 m^3. The temperature of the liquid ammonia at the end of the release was approximately -42°C. It is important to note that, during this test, minor leakages were observed at the bottom of the retention dike. In addition, part of the liquid ammonia was projected outside the retention dike under the effect of the velocity of the jet on the ammonia sheet. Liquid ammonia projections outside the retention tank were not accurately quantified.

photo 4: Vertical release in a $4m^3$ retention dike

In this way, it is possible to estimate that, at the end of the release, the quantity of liquid ammonia present in the retention tank was greater than 1520 kg, which represents approximately 65% of the total mass quantity released.

In addition, the liquid ammonia in a retention dike is not evaporated quickly. In fact, ammonia needs a significant quantity of heat to vaporise. It obtains this energy from external sources (temperature of ambient air, wind velocity, solar radiation, rain, etc.), and by lowering its temperature. In this way, during test 9, the temperature of the liquid ammonia fell from -40℃ at the end of the release to -60℃ one hour afterwards (temperature reached much more quickly for the other tests).

It is difficult to compare the progression of the ammonia concentrations leeward from releases impacting into a retention dike with impacting releases with no retention dike, because:

- The measurements made during test 8 (change of wind direction) are insufficient to compare with test 8b;
- in test 9, a decline in the ammonia concentration values over time is observed;
- and the weather conditions are different for the different tests.

The figure below represents the progression of the ammonia concentration measured in the near field 20 m from the release point over time for test 9.

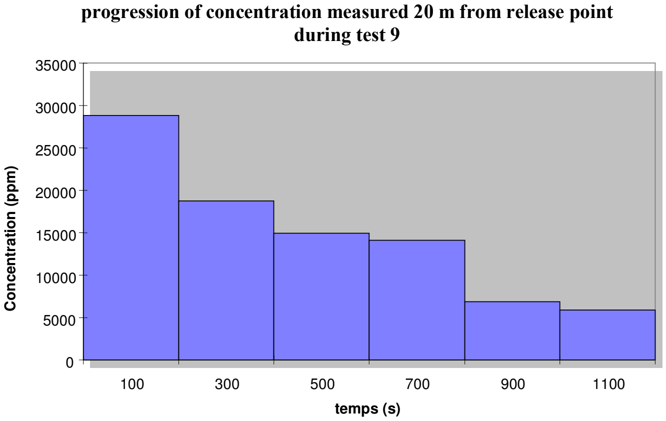


figure 28

In this figure, a mean of the ammonia calculation values was calculated on the basis of the measurements made every 200 seconds.

The decline in the ammonia concentrations over time for test 9 can be interpreted as follows. At the start of the release, the liquid ammonia impacting the retention dike is vaporised very quickly due to the energy supplied by the concrete contained in the retention tank. Over time, the temperature falls progressively, enabling the retention of liquid ammonia and the decrease in the quantity of ammonia vaporised over time.

In this way, a retention tank may represent an effective means to reduce the concentration level in the environment following a release, provided it is suitably positioned and designed. In particular, it is important to note that a retention dike installed under a leakage point may prove to be ineffective if the jet does not impact it directly or indirectly following an impact on an obstacle.

In addition, the retention dike must be well-maintained. In particular, the presence of water must be prevented as the water would provide additional energy to vaporise a larger quantity of liquid ammonia.

6.2.5 Influence of water curtain produced using peacock tail hoses

During this test campaign, two releases used peacock tail hoses installed on the release path. For these two tests, referenced 10 and 11, two 70 mm diameter peacock tail hoses were located 25 m and 60 m from the release point, respectively, as described in chapter 4. The purpose of these two tests was to try to evaluate the influence of the presence of a water curtain on atmospheric dispersion.

To study this influence for each of the two tests, we produced an open-field release for approximately 10 minutes. In order to be able to compare the ammonia concentration value results under atmospheric dispersion conditions which were as similar as possible before and after the start-up of the peacock tail hoses, we started up the peacock tail hose only 5 minutes after the start of the release.

On analysing the results, it has emerged that significant fluctuations in the atmospheric conditions were recorded during the tests, particularly the wind direction, which did not remain constant. In this way, during the tests, the ammonia plume sometimes passed by the water curtain.

In addition, under our release conditions during test 10, the ammonia jet passed through the water curtain located at 20 cm, rendering this type of curtain practically ineffective. At times, the jet was pointing towards the peacock tail in which the water was output at its highest velocity. Under these conditions, mechanical mixing of the plume could be observed as the jet was deviated from its path. However, during this test, the cloud generally passed between the two peacock tails, meaning that the concentration at the centre of the plume was not affected very much.

As an illustration of the previous pages, the graph in the figure below shows the progression of the mean ammonia concentrations leeward from release 11 before and after the start-up of the water curtain.

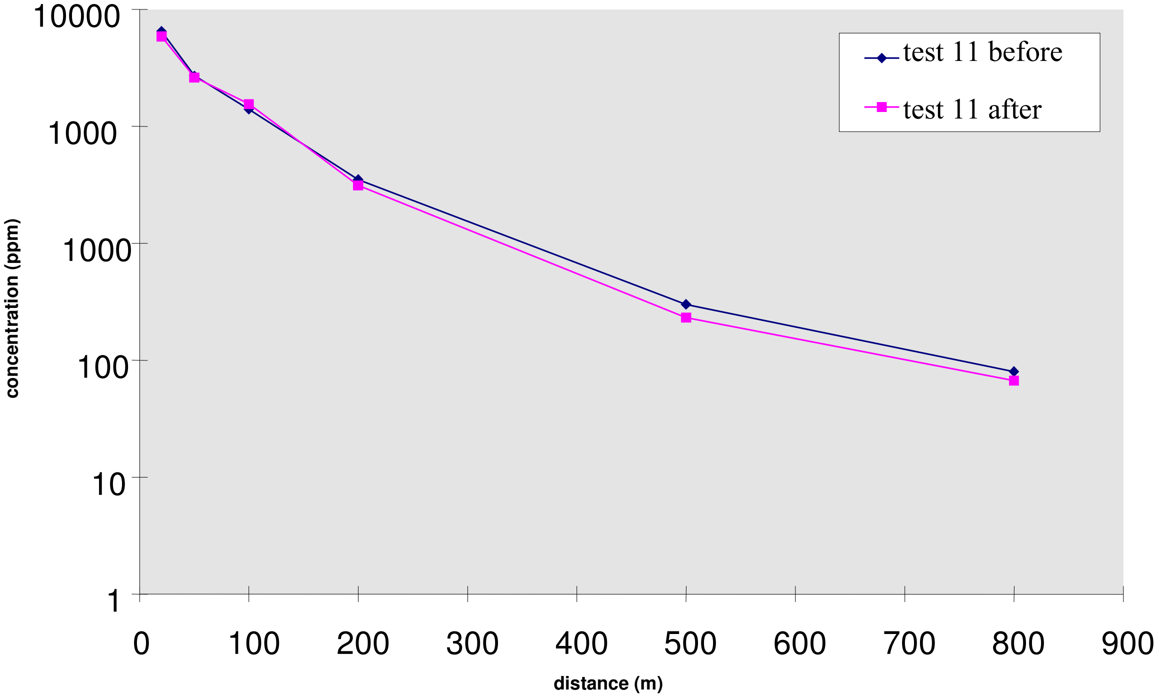


figure 29: Progression of ammonia concentrations leeward from release 11 before and after starting up the peacock tails

In the above figure, it is noted that there are no major difference before and after the peacock tails were started up. However, it is important to note that these concentration values are a factor in the direction adopted by the cloud.

In addition, it is important to note that, during test 11, the wind was relatively strong. The mean wind velocity was 5 m/s, with maximum velocities of 9 m/s recorded. During this test, the water curtain itself was flattened under the effect of the wind.

In this way, in this test campaign, the presence of a water curtain produced with peacock tail hoses did not significantly decrease the concentrations before and after the water curtain. This may be explained by the fact that an ammonia jet can pass through a water curtain if the momentum is sufficient, and by changing weather conditions during the tests. A release of the same type as those used in these test campaigns, but with a much lower momentum when passing through the water curtain may result in lower concentration values in the environment. This point is worth studying in more detail.

6.2.6 Experiment / modelling comparisons

In this section, the experimental results obtained during the test campaign were compared to calculation results obtained using a software program used to evaluate the effects of the accidental atmospheric release of toxic or flammable substances. This type of software program particularly makes it possible to calculate the dispersion of these substances in the atmosphere.

Of the software available, PHAST software version 4.2 was used. This model is of the integral type, i.e. it can be used to solve conservation equations based on simplifying hypotheses. With this respect, the limitations inherent to this software are particularly as follows:

- the site must be flat, of uniform roughness and not obstructed with obstacles ;
- the wind velocity must be at least equal to 1 m/s to obtain plausible results ;
- the weather conditions must be invariable throughout the emission and dispersions time ;
- the release source term must be constant over time.

To make the dispersion calculations for a substance in the atmosphere, it is necessary to define the source term of the release and the weather conditions in which it is dispersed in the model beforehand.

In chapter 5, we saw that the determination of the source term of a release with a model could give different results to that measured in reality. In order to do away with the source term problem (the subject of this section being the study of dispersion in the atmosphere), the comparisons were made as follows. Firstly, the parameters measured in the tank for a given release were entered in the software and, secondly, the other parameters such as the regular and irregular pressure drops were adjusted so as to calculate a mass flow rate identical to the flow rate measured experimentally.

Then, the meteorological data measured during the test were entered on the basis of the experimental data (ambient temperature, relative humidity, etc.). The mean wind velocity during the test was selected for the calculations. With respect to the atmospheric stability, we selected those which were calculated using the two methods described in chapter 5. If the two methods gave different stability classes, both classes were used for the calculations.

With these conditions entered in the software, firstly, we calculated the dispersion of ammonia in the atmosphere for open-field releases, i.e. tests 1, 2, 2b, 4, 10, 11 and 12.

The 4 graphs given in the figure below show a comparison between the experimental results (blue curve) and the results of dispersion calculations in the atmosphere.

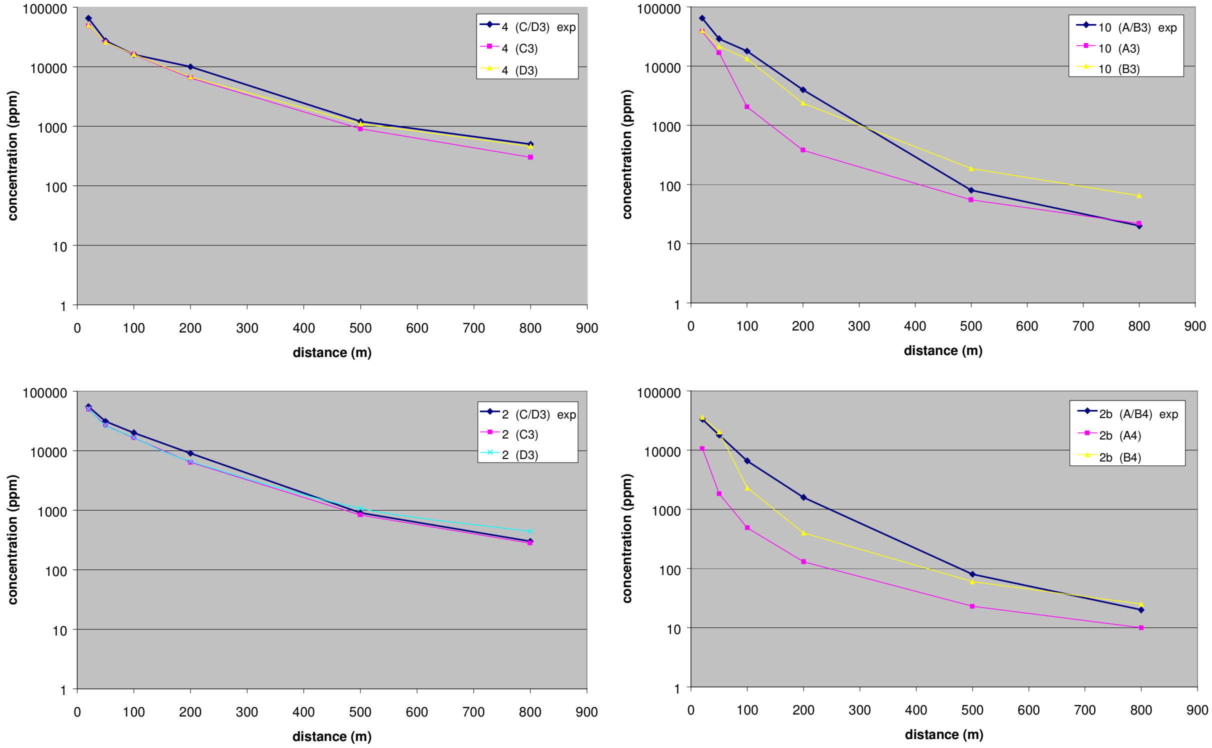


figure 30: Comparisons between calculation results and experimental results for tests 4, 10, 2 and 2b

In these graphs, it can be seen that the software calculates ammonia concentration values of the same order of magnitude as the values measured experimentally. Only test 2b, among the open-field releases, resulted in the calculation of two concentration values 100 m and 200 m from the release point which were significantly lower than the experimental values.

However, as a general rule, the modelling of the dispersion in the atmosphere of a liquefied gas release such as ammonia gives comparable orders of magnitude to that observed for large-scale releases, provided that:

- the source term is determined correctly in the software ;
- the weather conditions are defined correctly, given that they may vary rapidly over time (both the wind velocity and the atmospheric stability ;
- the release is carried out horizontally, in the direction of the wind, on a flat site and with no obstacles.

Secondly, we made calculations with impacting releases. The figure below shows the progression of the experimental concentrations (blue curve) and the concentrations calculated with the model for releases against a wall (tests 5 and 6) and on the ground (tests 7 and 8b).

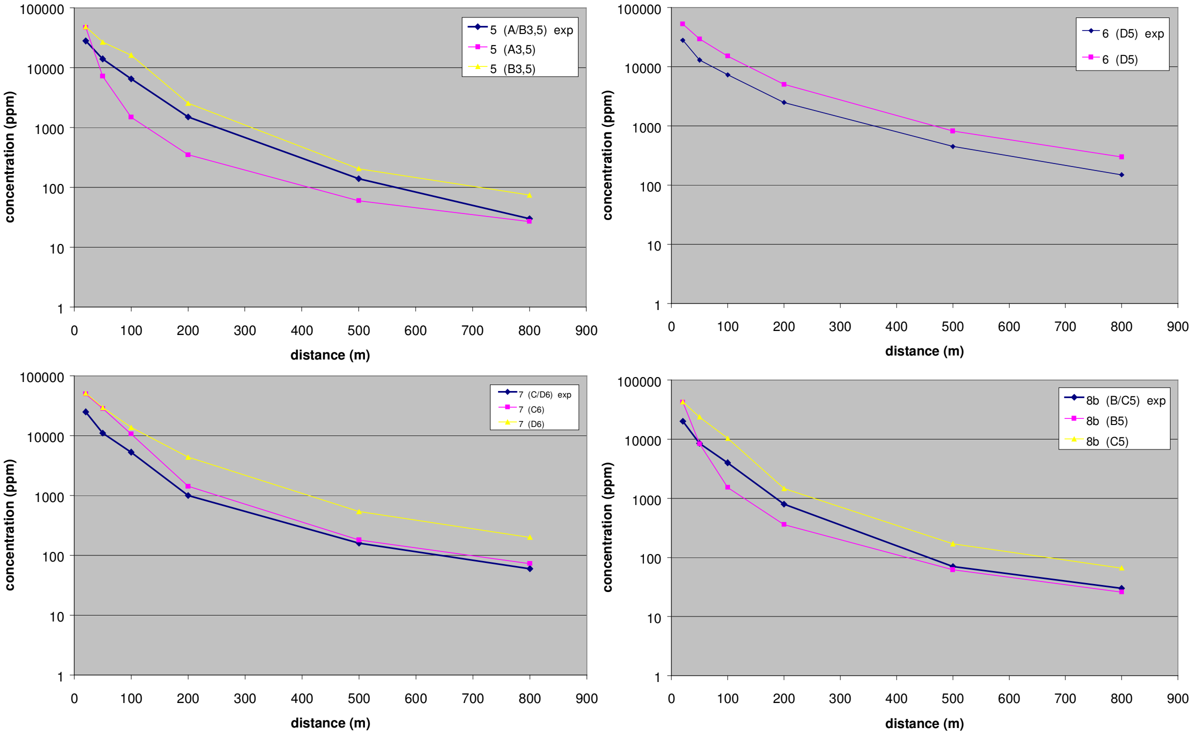


figure 31: Comparisons between calculation results
and experimental results for tests 5, 6, 7 and 8b

In this figure, it can be seen that, 20 m from the release point, the model systematically calculates a concentration approximately two times greater than that measured experimentally. Then, the progression of the concentrations depends on the atmospheric conditions. For test 6, in which these conditions were probably (D; 5 m/s) type, both curves (experimental and calculated) always show the same difference during the progression of the cloud leeward from the release. The mixing of the cloud following the impact of the release, on one hand, and the retention of ammonia at the release point, on the other, may explain this difference.

At the present time, integral type models do not account for releases impacting solid surfaces. Differences of the order of 50% may be observed between large-scale test results and calculations made with this type of model. Even greater differences may be observed if the configuration of the impact is complex or if a retention dike is suitably positioned with respect to the release.

7. CONCLUSION AND PROSPECTS

Within the scope of this research programme, INERIS essentially conducted a test campaign in order to improve knowledge on the atmospheric dispersion of ammonia, particularly in open or obstructed environments.

Of all the results obtained from this test campaign, the following points are worth noting:

- 15 tests with different configurations were conducted over the period between December 1996 and April 1997 ;
- the quantity of ammonia released from the liquid phase was, depending on the tests, between 1400 kg and 3500 kg per test over a time of between 7 and 14 minutes, i.e. flow rates between 2 and 4.5 kg/s ;
- in the case of the thermodynamic progression of ammonia in the tanks, temperature and pressure measurements were made during the releases. These measurements and the interpretations are given in chapter 5 ;
- in the case of the thermodynamic progression of ammonia in the pipes, the measurements made at the same point demonstrated that the value of the pressure is similar to the saturating vapour pressure corresponding to the temperature measured at this point ;
- approximately 200 sensors, to measure the ammonia concentration and the temperature, were set up for each test ;
- the ammonia cloud formed behaves like a heavy gas, and no rise in the cloud is observed ;
- the temperature in the ammonia jet can typically fall to -70℃ ;
- solid obstacles (wall or ground) placed in a two-phase ammonia jet at a distance of a few metres from the release point have a major influence on the concentration values measured after the obstacle. In this test campaign, approximately two times lower concentrations were measured after the obstacle with respect to an open-field release ;
- If the release is pointed towards the retention dike, the dike can retrieve a large quantity of ammonia in liquid form. For two tests, quantities greater than 50% of the total mass released were collected in liquid form at a temperature of approximately -60℃ ;
- The liquid ammonia sheet formed in this way is not evaporated rapidly ;
- water curtains produced with peacock tail hoses and located on the plume path had little effect on ammonia dispersion under the test conditions ;

- in addition, the results obtained demonstrate that the integral type dispersion models currently available can give correct orders of magnitude of concentrations leeward from a free release. In the case of an impacting release, the results obtained are only correct if the models receive information beforehand on the quantity released into the atmosphere (in vapour or aerosol form) after the impact.

The results obtained during these tests led us to develop a new programme intended to study the "near-field dispersion of a liquefied gas in the presence of obstacles". The purpose of this programme, initiated in 1999 at INERIS, is particularly to create a mathematical model used to account for the interaction of a liquefied gas release against an obstacle. In the long-term, this model could be incorporated in integral type software.

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9. LISTE DES ANNEXES

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Appendix 2	Main direct measurement techniques	6

APPENDIX 1

THERMOCOUPLE INDICATION

The thermocouples referred to in this appendix are those which were installed:

- in the ammonia tank,
- on the release system,
- on the release slab,
- and, if applicable, on the wall or retention dike.

A description of the location of the thermocouples is given in the table below.

For all the tests, the following thermocouples were installed:

Thermocouple location	**Caption**
in tank 1450 mm from base	Tank 1450 mm
in tank 1100 mm from base	Tank 1100 mm
in tank 750 mm from base	Tank 750 mm
in tank 400 mm from base	Tank 400 mm
in tank 50 mm from base	Tank 50 mm
at end of release system	OUTLET – th6
between two release system valves	th 7
at inlet of release system	th 8

Test 4:

For this test, four additional thermocouples were installed on the ground. Two in the direction of the release 3 and 5 metres from the orifice and two on either side at 3 metres.

Thermocouple positions	**Caption**
on ground, in direction of release (27), 3 metres from orifice	ground dir 27 at 3m
on ground, in direction of release (27), 5 metres from orifice	ground dir 27 at 5m
on ground, in direction of release (23), 3 metres from orifice	ground dir 23 at 3m
on ground, in direction of release (31), 3 metres from orifice	ground dir 31 at 3m

Tests 5 and 6:

With respect to these tests, a 3 metres wide, 3 metres high and 1 metre thick wall was constructed at a distance from the orifice of 3 metres and 1 metre, respectively. For both configurations, 19 thermocouples were installed, 4 on the wall and 15 on the ground.

On the wall, the 4 thermocouples referenced 11 to 14 were installed as described in figure 32 below.

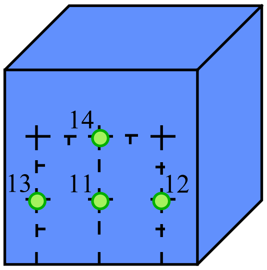


figure 32

For test No. 5, the thermocouples were installed on the ground as described in figure 33.

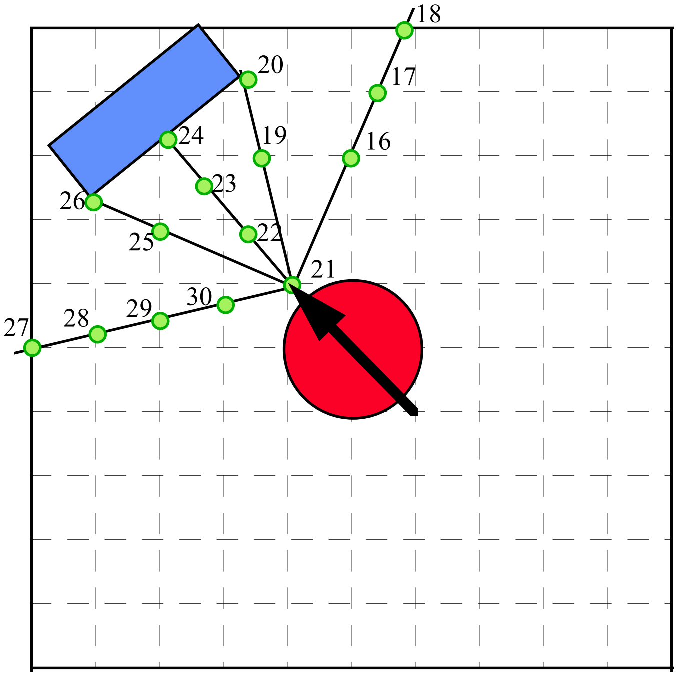


figure 33

The caption used for each of these thermocouples is given in the table below.

Caption	
th11 – wall 1 m centre	th21 – ground centre
th12 – wall 1 m right	th22 – ground centre
th13 – wall 1 m left	th23 – ground centre
th 14 – wall 2 m centre	th24 – ground centre
th16 – ground 60° right	th25 – ground 30° left
th17 – ground 60° right	th26 – ground 30° left
th18 – ground 60° right	th27 – ground 60° left
th19 – ground 30° right	th28 – ground 60° left
th20 – ground 30° right	th29 – ground 60° left
th30 – ground 60° left	

For test 6, the wall was located one metre from the release system orifice. Therefore, the thermocouples were installed on the ground as shown in figure 34 below.

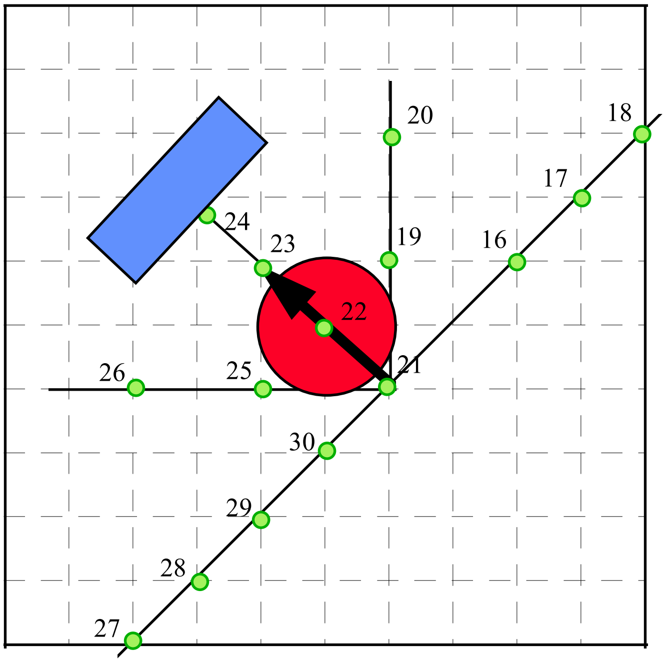


figure 34

Tests 7 and 8: These tests were instrumented as follows (see figure 35):

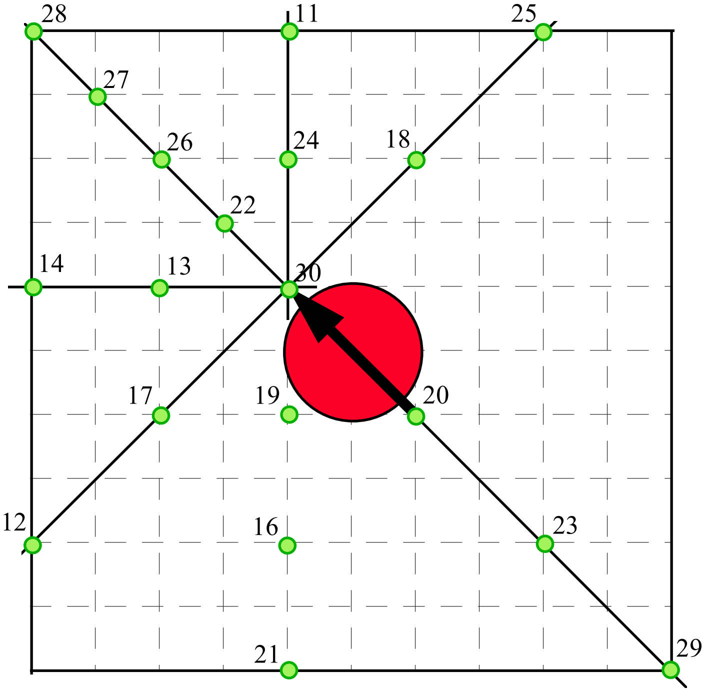
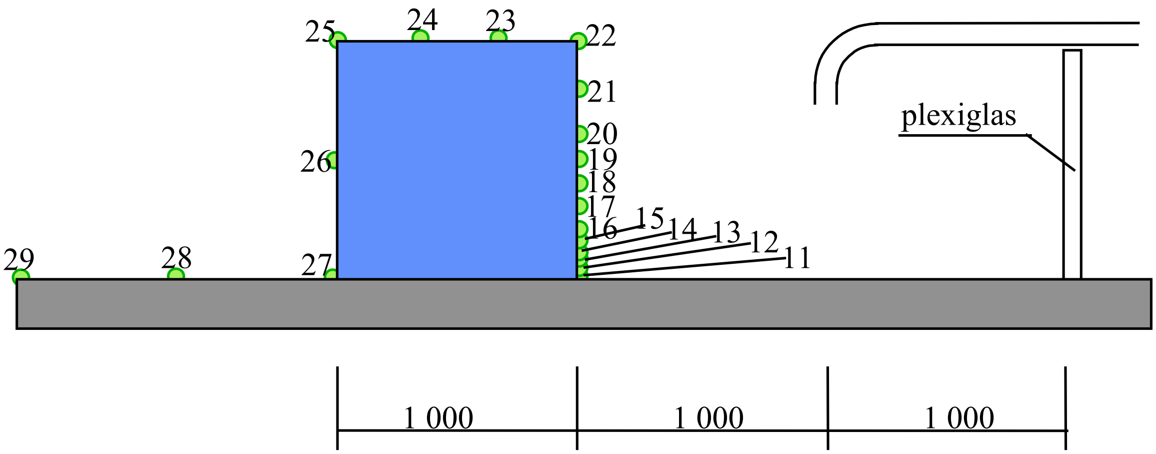


figure 35

Test 9:

For this test, the end of the release system impacted into a 2m x 2m x 1m retention dike. The thermocouples were installed along the direction 20, as described in the figure below.



height / ground (mm)	thermocouples			
0	th11	th27	th28	th29
30	th12			
60	th13			
100	th14			
150	th15			
200	th16			
300	th17			
400	th18			
500	th19	th26		
600	th20			
800	th21			
1000	th22	th23	th24	th25

Tests 10, 11 and 12:

For these three tests, 6 thermocouples were installed on the ground along the axis of the release system. From the vertical line from the release point, there was one every metre. We indicated them as follows:

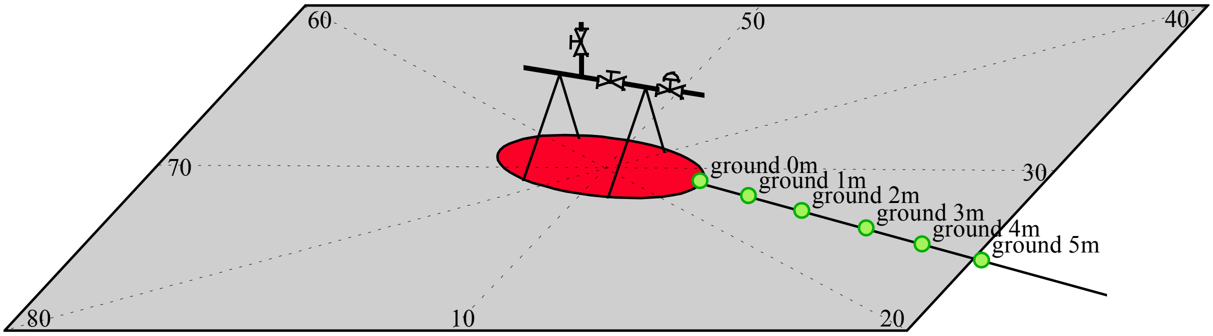


figure 36

Tests 2b and 8b:

For these two tests, in addition to the 6 thermocouples described above, we installed 12 on two masts, and 1 to 50 cm above the release orifice. The latter is indicated in the caption: "point 0 – h=1.5m". The other thermocouples are indicated as follows on masts 1 and 2, located 2 and 4 metres from point 0 in the direction 7, respectively.

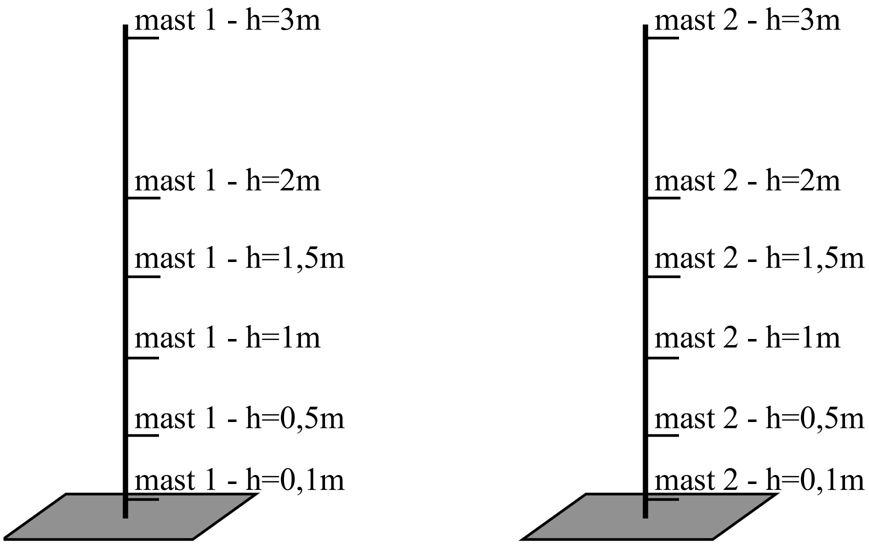


figure 37

APPENDIX 2

MAIN DIRECT MEASUREMENT TECHNIQUES

The purpose of appendix 2 is to give a brief presentation of the main ammonia concentration measurement techniques. This chapter is particularly based on the work by A. Accorsi's team [1,3] and the documentation supplied by the manufacturers, particularly [2,4].

1 ELECTROCHEMICAL CELL DEVICES

This section is essentially based on document [1].

Device to measure gas concentrations in the air using electrochemical cells emerged approximately twenty years ago.

Measurement principle

Each electrochemical cell is relatively specific for the detection of a single gas. The gas to be measured passes through a semi-permeable membrane, i.e. permeable for gases but impermeable for liquids. The gas comes into contact with a sensitive electrode coated in a catalyst in the presence of which, it is oxidised, while a counter-electrode reduces the oxygen in the air. These oxidation-reduction phenomena are accompanied by an ion flow through the electrolyte and an electron flow to the outside. (See Figure 2.1)

The reaction to the sensitive electrode is (according to MARTEC documentation):

$2\ NH_3$ --------> $N_2 + 6\ e^- + 6\ H^+$

The reaction to the counter-electrode is (according to the CECA report):

$2\ e^- + 0.5\ O_2 + 2\ H^+$ -------> H_2O

Overall:

$2\ NH_3 + 3/2\ O_2$ -------> $N_2 + 3\ H_2O$

To avoid capacitive limit layer phenomena at the electrode/electrolyte interface, a reference electrode maintains the potential of the sensitive electrode at a fixed value, which makes it possible to keep a signal stable over time.

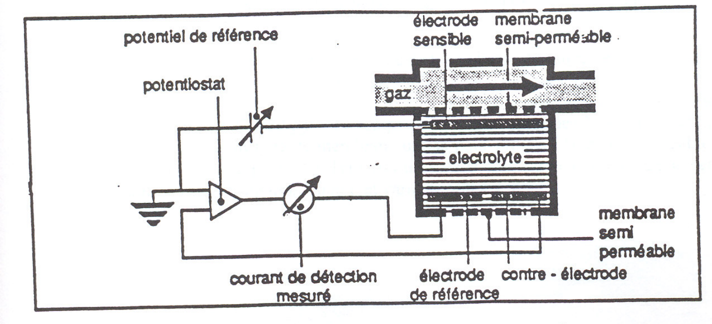


Figure 2.1: Functional description of an electrochemical cell
(diagram p 44 fig. 5 in CECA report [1])

Limitations

Selectivity is obtained, firstly, with the value of the reference potential and, secondly, with the oxidation catalyst. In practice, absolute selectivity does not exist. For example, the table below, given by Dräger, shows some compounds inducing interference on PAC II NH_3:

Gas	Symbol	Test gas concentration (V/V)	Deviation in ppm NH_3 from measurement value
Chlorine	Cl_2	10 ppm	< 1
Cyanhydric acid	HCN	25 ppm	< 3
Carbon dioxide	CO_2	1%	-5 < and < 0 (default signal)
Carbon monoxide	CO	115 ppm	< 3
Methane	CH_4	30%	< 3
Methanol	CH_3OH	170 ppm	< 35
Sulphur anhydride	SO_2	20 ppm	<1
Hydrogen sulphide	H_2S	20 ppm	< 75
Nitrogen dioxide	NO_2	20 ppm	< 3
Hydrogen	H_2	1.53%	< 115

Table 2.1: Compounds inducing interference on PAC II NH3, based on Dräger's technical documentation for PAC II NH3

In this way, it is difficult to know exactly what is being measured and, in particular, how accurate the measurement is, in the case of an environment in which several gases are present (for example, in industrial atmospheres).

The measurement range of the majority of electrochemical type devices, for measuring ammonia concentrations, is from a few ppm to 300, 500 or 1000 ppm. Cells capable of measuring around one thousand ppm are very rare. The limit of detection is of the order of 20 to 30 ppm. The response time is in excess of 20 s and may be up to one minute, and depends on the type of membrane used to protect the sensitive electrode. The service life of this type of device is approximately one to two years. The average price of an electrochemical cell alone is approximately 1000 FF and varies from 500 to 7000 FF.

2 CATALYTIC OXIDATION DEVICES (PELLISTOR)

This section proposes a summary of the EEV [2] and INRS [3] technical documents.

Principle

The principle consists of inducing the catalytic oxidation of the flammable gas, in this case, ammonia, and measuring the heat produced.

In fact, the catalytic detector is equipped with two components: an active catalytic detector and a non-active compensator component. Each component consists of a platinum filament in a bead of heat-resistant material. For the detector component, a catalytic mixture is applied to this bead, while for the compensator component, the bead is treated such that catalytic oxidation cannot occur.

The two components are connects in a Wheatstone bridge as shown in figure 2.2 taken from the document [3].

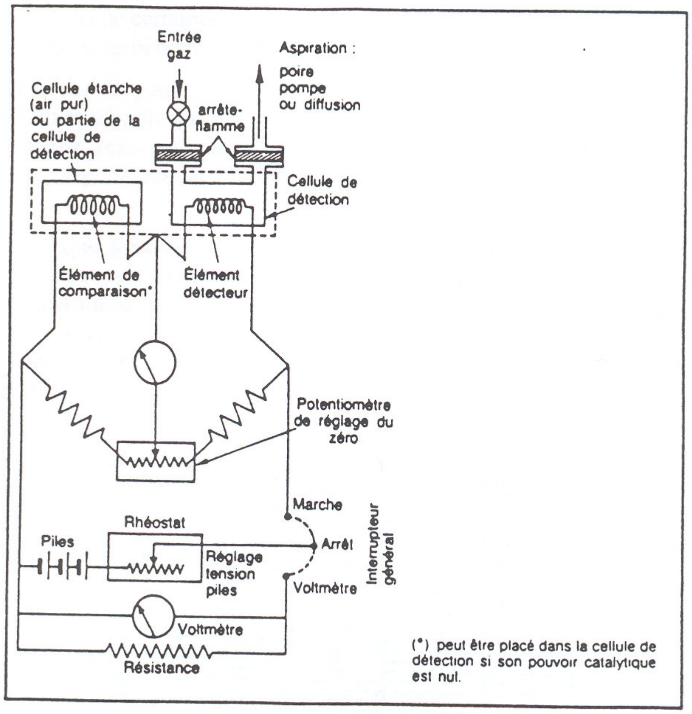


Figure 2.2: Principle diagram of catalytic oxidation measurement device
(INRS diagram)

The direct current flowing through the beads brings the detector to a suitable temperature for the gas to be detected. The detector filament works like a thermometer: when the combustible gas is oxidised on the detector bead, the resulting temperature rise increases filament resistance. This unbalances the bridge, giving a signal that can be read, either as a gas percentage, or as a percentage of the Lower Explosibility Limit (LEL), or that triggers an audio or visual alarm.

The rate at which the gas will burn on the detector component depends on the gas diffusion rate in the detector. The diffusion rate is controlled by enclosing the components in a unit of precise dimensions.

In addition, EEV explains that there are two assembly arrangements. In the first, the gases circulate at a given flow rate of 0.5 litre/minute. The second arrangement is designed for simple gas diffusion in a unit. In both cases, a frit is included and a paper filter is placed in the diffusion head to prevent dust from penetrating into the cavity. Another possibility consists of replacing the frit with a disk of tiny bronze or stainless steel beads (recommended for ammonia).

Limitations

The service life of the detector is limited. It is associated with the operating temperature, and also with a loss of efficiency over time, which depends on prolonged operation, exposure to excessively high concentrations. Finally, the detector may be damaged ("poisoned") by some gases or vapours. To protect the detector from the effects of some organic or silicone-based vapours, an interchangeable activated charcoal or carbon filter may be used.

The bridge output signal is of the type represented in figure 2.3. It rises above the LEL (Lower Explosibility Limit), up to the stoichiometric value which is approximately 10% in air for methane (example represented below) and 21% for ammonia. For higher concentrations, the signal declines in a linear fashion due to the lack of oxidant.

It can be noted that, when the combustible gas concentration exceeds the stoichiometric value, it is possible to use another type of detector based on the thermal conductivity principle to measure high concentrations and thus eliminate any doubt with respect to ambivalence. As such, the compensator components of some catalytic oxidation detectors may be used. However, according to the information supplied by EEV, the thermal conductivity of ammonia is very similar to that of air, so much so that it may be impossible, or very difficult, to make an accurate, detailed measurement.

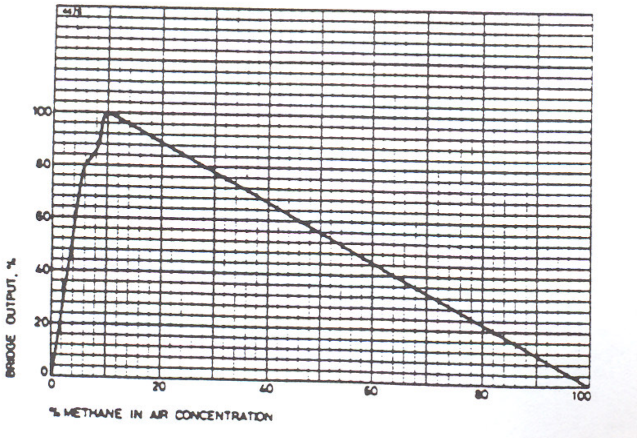


Figure 2.3: Pellistor type sensor output signal for exposure to methane
(diagram from EEV brochure)

Concentrations greater than the stoichiometric value may be measured by diluting with air according to a known dilution ratio, e.g. 10. In this way, 100% v/v ammonia would be lowered to 10% and the detection sensitivity would be of the order of 1% v/v.

3 SEMICONDUCTORS

The documents [3,4] were used to prepare this section.

Principle

A semiconductor is a material in which the electricity conducting properties are intermediary between those of a conductor and those of an insulator. The presence of a gas induces a variation in the electrical resistance of the semiconductor components of the detector by means of physical adsorption (reversible phenomenon) and catalytic combustion phenomena on the semiconductor surface; the adsorbed gas is oxidised in the presence of surface oxygen and the combustion product is desorbed. Modifying the oxygen content on the surface induces a modification in the electron-hole equilibrium (the hole being the adsorption site) in the semiconductor. This variation is directly linked with the gas concentration and modifies the electrical equilibrium of the circuit in which the detector is placed.

In the case of the Figaro detector, the semiconductor material used is tin dioxide (SnO_{2-X}) which is heated to a high temperature (e.g. 400℃).

Limitations

Semiconductor detectors are very temperature-sensitive: the conductibility increases with the temperature. In addition, semiconductor operation is disturbed by interfering parameters such as humidity, dust, grease of other preferentially adsorbed gases.

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[2] EEV. Combustible Gas Detectors – Product Data

[3] A. Accorsi, J. C. Laforest, P. Huré. Détection de mélanges air-ammoniac. INRS. Cahiers de notes documentaires n°127, p 217-222, 2e trimestre 1987.

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