CONTENTS

Analysis of accidental cases

GLOSSARY

LP Low Pressure.

C.F.C. Chloro-Fluoro-Carbon.

G.W.P. Global Warming Potential. The GWP is a substance's earth warming potential by comparison with that of CO_2. This value is strongly effected by the time period considered (20, 100, 500 years, etc.).

H.C.F.C. Hydro-Chloro-Fluoro-Carbon - Alternative transition fluid.

H.G.W.P. Halocarbon Global Warming Potential. A substance's greenhouse effect in relation to that of R11.

H.F.A. Hydro-Fluoro-Alcane (or FORANE equivalent to H.C.F.C. in France).

H.F.C. Hydro-Fluoro-Carbon - The alternate fluid of the future, containing no chlorine (O.D.P. = 0) although does have a greenhouse effect.

HP High Pressure.

O.D.P. Ozone Depletion Potential (index characterising a molecule's participation in the destruction of the ozone layer).

R11 C.F.C. - Trichlorofluoromethane (CCl_3F).

R113 C.F.C. - Trichlorofluoroethane (CCl_2F-$CClF_2$).

R114 C.F.C. - Dichlorotetrafluoroethane ($CClF_2$-$CClF_2$).

R115 C.F.C. - Monochloropentafluoroethane ($CClF_2$-CF_3).

R12 C.F.C. - Dichlorodifluoromethane (CCl_2F_2).

R13 C.F.C. - Monochlorotrifluoromethane ($CClF_3$).

R13B1 C.F.C. - Trifluorobromomethane (CF_3Br).

R134a H.F.C. - (1^{st} alternate fluid for R12).

R152a H.F.C. - Difluoroethane (CH_3-CHF_2).

R22 H.C.F.C. - Monochlorodifluoromethane ($CHClF_2$).

R23 H.C.F.C. - Trifluoromethane (CHF_3).

R404A H.F.C. - (substitute for R502).

R500 C.F.C. - Azeotropic mixture (73.8% R12 and 26.2% R152a).

R502 C.F.C. - Azeotropic mixture (48.8% R22 and 51.2% R115).

R503 C.F.C. - Azeotropic mixture (59.9% R13 and 40.1% R23).

R717 Anhydrous ammonia ("refrigerant quality", 99.95% minimum purity).

T.E.W.I. Total Equivalent Warning Impact (index characterising the refrigeration system's impact on the greenhouse effect).

INTRODUCTION

History

The first practical refrigeration machine appeared in the middle of the last century following a patent filed by Jacob Perkins in 1834 concerning a vapour compression system[1].

Cold was produced artificially for the first time in 1857. At the Universal Exposition in London, Ferdinand Carre presented an absorption-type machine which made ice cubes almost continuously. The machine used ammonia as a refrigerant and water as the absorption substance. In 1874, Pictet built the first compression machine. His machine used sulphur dioxide (SO_2), while Lowe, in the United States, manufactured comparable machines that operated on carbon dioxide (CO_2).

Ammonia was used for the first time in a vapour compression machine built by Carl Von Linde in 1876. Following the Paris Universal Exposition of 1878, the majority of large breweries began using ammonia compression systems. In 1876, a Frenchman by the name of Charles Tellier equipped a 650-ton ship (the "Frigorifique") to transport a cargo of frozen meet to Buenos Aires in 3 months and in excellent condition[2]. Quick-freezing, as it is practiced today, was invented in 1929 by an American, Clarence Birdseye, who filed a patent concerning quick-freezing of perishable foodstuffs.

Numerous refrigerants were used such as dimethyl ether, which is explosive and was rapidly replaced by ammonia, carbon dioxide, sulphur dioxide, propane and methyl chloride (CH_3Cl) [3]. In the early 20th century, the need for refrigeration increased. This development was associated with a growth in agricultural production and a new activity sectors which called upon refrigeration techniques (the dairy, meat processing industries, and the maritime transport of perishable foodstuffs). The competition between the various refrigerants increased.

---

1 L'ammoniac utilisé comme frigorigène, *Ammonia used as coolant* (INTERNATIONAL INSTITUTE OF REFRIGERATION I.I.R. - 1993).

2 Petit livre bleu des surgelés des glaces, *Small blue book of quick-frozen foods, ice cream* (Ficur - 1987).

3 La sécurité et l'ammoniac, *Safety and ammonia* (Magazine Générale du Froid, No. 74 / G. VRINAT - June 1990).

The uses of ammonia and carbon dioxide varied according to the country, although in the 1920's, ammonia progressively took precedence in large industrial installations and on board ships. Low power installations use sulphur dioxide and methyl chloride in particular.

It wasn't until the 1930's and the development of domestic refrigeration that the American company, Kinetic Chemicals, developed chloro-fluoro-carbon (C.F.C.) synthetic fluids whose high molecular mass is well suited to centrifugal compression and allowed the development of hermetic compressors[3/4]. C.F.C.s then progressively replaced methyl chloride, CO_2 and SO_2. The main C.F.C.s are essentially[5]:

- R12 (CF_2Cl_2) for applications in the vicinity of 0°C and especially the air-conditioning of occupational settings, industrial heat pumps, and the refrigeration and storage of fresh foodstuffs,
- R11 ($CFCl_3$) used in centrifugal machines,
- R502 (a mixture of R22 / $CHClF_2$ and R115) for low temperatures such as freezing and the storage of frozen foods and ice cream products. This refrigerant is also used in "frozen food display cases" in supermarkets and hypermarkets.

Current situation and perspectives

In 1974, the American chemist, F. Sherwood Rowland, postulated a significant destruction of the ozone layer in the upper atmosphere by the chlorine contained in C.F.C.s. In the autumn of 1987, a "hole" was detected in the ozone layer above Antarctica. This anomaly is attributed, at least partly, to C.F.C.s. The international community decided to limit their production and to prohibit them once and for all as of January 1st, 1996 (the Vienna Convention in 1985, the Montreal Protocol in September 1987, the London Agreement in 1990 and the Copenhagen conference in 1992). Excluding new materials and techniques, this common position of the governments had two consequences:

- for the upcoming years, the main producers of C.F.C. propose substitute refrigerants such as hydro-chloro-fluroro-carbon compounds (H.C.F.C.) or hydro-fluoro-alcanes (H.F.A. or FORANE, in France), less aggressive transition fluids, and are searching for new totally neutral molecules in the long term,

---

4 Production du froid - Technologie des machines industrielles, *Cold production - Technology of industrial machines*
(Les Technologies de l'Ingénieur / Georges VRINAT).

5 SAVE summer training program - Club M3E (Association Française du Froid /A.F.F. G. VRINAT - 1994).

The main H.C.F.C. is R22, which is widely used in industrial type food freezing and storage installations,

- the return of old refrigeration fluids and essentially ammonia...

Ammonia can be used in the majority of industrial refrigeration, freezing installations and stores at all temperatures.

Refrigerants have a double effect on the environment[5/6]:

- effect on life forms characterised by the O.D.P. (ozone depletion potential),
- effect on the climate characterised by the H.G.W.P. (hydrocarbon global warming potential) and the T.E.W.I. (impact with relation to CO_2).

Refrigerant	**Ozone ODP/R11**	**Greenhouse effect HWP**	**TEWI/CO2 20 year period**	**TEWI/CO2 100 year period**	**TEWI/CO2 500 year period**
R12	0.9 to 1	2.8 to 3.4	7,100	7,300	4,500
R502	0.17 to 0.28	4.02	4,820	4,260	4,040
R22	0.04 to 0.06	0.32 to 0.37	4,100	1,500	510
R717 (NH3)	0	0	0	0	0

Nowadays, industry uses refrigeration to a wide extent, to liquefy gases, condense volatile liquids, crystallise salts, control violent reactions or more simply... to preserve sensitive products from "heat" and perishable foodstuffs.

The economic impact of refrigeration techniques throughout the world is extensive[7/8]. The overall amount of yearly investments in refrigeration equipment is nearly 500 billion French francs, the value of the products preserved by cold would represent 10 times that amount. There is approximately 300 millions metric cubes of refrigerated storage capacity in the world, allowing to store 5% of the total annual product of foodstuffs at any given time. Considering retail trade, refrigerated transports and domestic appliances, 10 to 25% of the world's food production enters the "cold chain" at one stage or another.

Used for decades owing to its excellent thermodynamic properties and progressively replaced over the last twenty years, particularly by C.F.C.s (not thermally efficient

---

[6] Total Equivalent Warming Impact (T.E.W.I.) M. DUMINIL (Magazine Générale du Froid, No. 36 - October 1993).

[7] Ammonia used as coolant (INTERNATIONAL INSTITUTE OF REFRIGERATION I.I.R. / I.I.R - 1993).

[8] The CFC/Ozone problem and possibilities for emission reduction in Refrigeration, Air Conditioning and Heat Pump applications (DKV / Statusberich No. 2 - July 1987).

although non-toxic), ammonia is returning to the forefront as a calorific fluid little by little. In 1984, the world production of ammonia was 120 million tons; less than 5% of this production was used as a refrigerant under the code R717 (at least 99.95% pure).

Ammonia refrigeration units can be used in refrigerated storage or in certain sport complexes (ice skating rinks, etc.), for example. By their nature, these activities are often located in or near the urban fabric. An often-sensitive environment, the facility including the units concerned and the redevelopment of the use of ammonia as a potential substitute for C.F.C.s fully justifies this research study[9].

9 Appendices 1 and 2: Type and characteristics of industrial refrigeration installations / Current and alternative technologies.

LIQUEFIED AMMONIA

REFRIGERATING INSTALLATIONS

Cold production

General

Cold is produced by absorbing heat to a temperature below that of the ambient environment. The numerous processes used are habitually classified according to the type of basic phenomena that they use. We can thus distinguish [10]:

- the thermodynamic methods, which use endothermic phenomena accompanying the phase changes (fusion, sublimation, evaporation, expansion or dissolution) or certain chemical reactions,
- the electrical or magnetic processes, which slow down molecular agitation at the origin of the heat phenomena by subjecting refrigerant atoms to an electric current or a magnetic field.

Thermodynamic methods are the most popular. Cold is most often produced by the expansion of a compressed gas, generally of the FORANE (or FREON) family or by evaporation of a fluid with a low vapour tension, such as ammonia. The vast majority of systems using these methods implement a compression and expansion cycle, in a closed circuit, in which the fluid conveyed, essentially gaseous, may or may not undergo a phase change.

As the transfer of heat occurs spontaneously toward lower temperatures, the intermediate fluid is used after first lowering its temperature. It is thus referred to as a refrigerant.

---

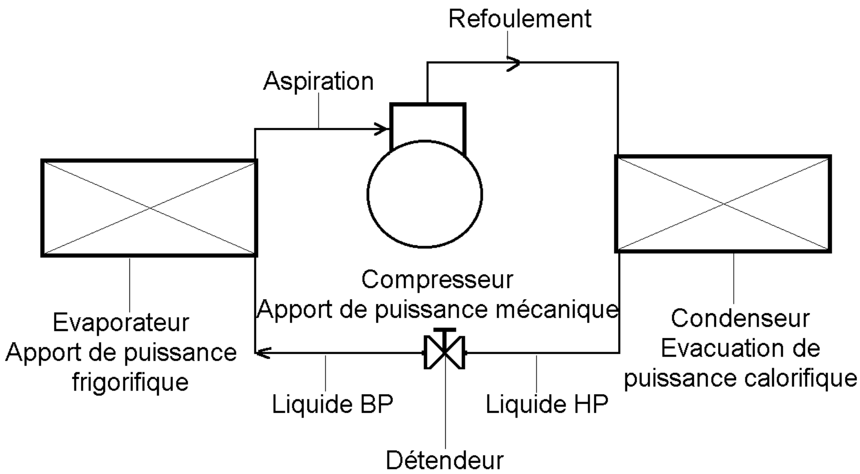
[10] 12 technologies pour l'avenir de l'environnement, *12 technologies for the future of the environment* (French Ministry of Industry and External Commerce / SRI International - 1992).

Theoretical refrigeration cycle

In order to absorb heat at low temperature (the useful part of the cycle!), the majority of processes that implement an intermediate fluid flow in a closed cycle to reproduce the refrigeration development of the entire system as many times as necessary.

Technical refrigeration is essentially produced by vapour compression systems. A vapour compression cycle features the following main elements:

- an evaporator, in which vaporisation of the refrigerant removes a quantity of heat Q_0 to the outside environment,
- a mechanical compressor that draws in the vapours formed in the evaporator at pressure P_2 to compress and expel them at pressure P_1. The compressor absorbs mechanical energy W,
- a condenser, in which the refrigerant condenses and releases a certain quantity of heat Q into the outside environment,
- a fixed expansion valve, through which the refrigerant flows to return to the evaporator, its pressure being brought from P_1 to P_2.



Refrigerating cycle flow diagram

A theoretical refrigeration cycle includes the following 4 phases:

- vaporisation of a fluid at constant pressure and temperature (P_2 & T_2), with absorption of a quantity of evaporated fluid heat (Q_0 / kg), borrowed from the outside environment of temperature $T_2' > T_2$ (cold production),
- adiabatic compression (without heat flow) of the humid vapour in a compressor which brings the pressure to the value P_1, and vapour tension of

the fluid to condensing temperature T_1. This compression absorbs a certain amount of work supplied by an external energy source,

- condensation of the fluid in the condenser, at pressure P_1 and temperature T_1, depending on the unit and the temperature T_1' of the external environment where the condensation heat Q_1 will flow (with naturally $T_1 > T_1'$),
- adiabatic expansion of the refrigerant in an expansion valve attached to the same shaft as the compressor to recover this expansion work of the pressure P_1 of the condenser to that of the evaporator P_2.

In order to translate these phenomena, the refrigeration industry often uses:

- either an enthalpy/pressure (H, P) diagram. The values used in the calculations, characterising the fluid state, are thus the pressure (P), the absolute temperature (T), the enthalpy (H), the specific volume (V), the titer (x) and the entropy (S),
- or an entropy diagram (S, T) in which a CARNOT ABCD cycle evolving between 2 isotherms (T_1 & T_2) and 2 adiabatics (AD and BC) represents the operation. The curves delineate different areas which correspond to the heat exhausted to the condenser (Q_1), to that absorbed by the evaporator (Q_2), to the work absorbed by the compressor, to that recovered in the expansion valve and to that consumed by the machine. A coefficient of performance ($T_2/(T_1-T_2)$) can then be calculated.

Actual refrigeration cycle

The actual refrigeration cycle of a machine can differ from the theoretical cycle depending on, for example, the various equipment installed on the installation (motor energy savers, etc.).

Compression refrigeration systems using ammonia as refrigerant

The design of refrigeration machines using ammonia or halogenated fluids is comparable. The components, however, are made of ordinary steel, as copper, copper alloys and zinc are attacked by ammonia. Considering its intrinsic characteristics and particularly its incompatibility with cupreous metals but also the market share that it currently represents, equipment adapted to ammonia is very specific and less widespread than its "halogenated fluid" type counterpart[11].

Finally, the intensive turn to halogenated fluids in all fields using refrigeration has resulted in the development of techniques that are more advanced than those required by

[11] SAVE summer training program - Club M3E (Association Française du Froid /A.F.F. G. VRINAT - 1994).

ammonia and simpler installation practices. Ultimately, the practices, inevitably more strict used for ammonia systems, are sometimes not or little known by installers [12].

A natural substance, ammonia is also synthesised in large quantities by the chemical industry. As a refrigerant, it has certain advantages and, in particular:

- good thermodynamic properties (heat/mass transfer) enabling machines with one of the best performance coefficients existing to be obtained. The mass over installed power ratio is in the order of 5.5 kg of NH_3/kW [13],
- a higher critical temperature,
- a higher vaporisation enthalpy, making it possible to produce temperatures as low as - 60°C,
- chemical neutrality vis-à-vis components of the refrigeration system, excluding copper and its alloys as well as reliability in the presence of humid air and water,
- better stability vis-à-vis oil,
- easy leak detection, even small leaks (olfactory detection at 5 ppm, etc.),
- it has no atmospheric ozone effect or greenhouse effect contribution,
- the lowest purchase price of all refrigerants (5 to 8 times cheaper per kg, 11 to 17 times when the reduction in installation size is taken into account),
- reduced pumping cost for embedded systems and reduced piping dimensions for the same refrigerating power,

  In relation to the other refrigerants and at equal energy efficiency, a lower mass flow (proportional to the mole weight of the fluid), piston speed from 2.5 to 3.2 times greater [14] (inversely proportional to the square root of this weight), as well as greater heat transfer at the evaporation/condensation stages (linked to the lightness of ammonia) and finally, better thermal conductivity (point 1 above), all lead to lower production costs for an installation[15].

The restrictions associated with its use are due to the related hazards, and in particular:

- a potential character as an flammable gas,
- the strong exothermicity of its dissolution in water,
- its toxicity at low concentrations in air (25 ppm),

---

[12] La sécurité et l'ammoniac, *Safety and ammonia* (Magazine Générale du Froid, No. 74 / G. VRINAT - June 1990).

[13] Guide d'étude des risques technologiques, *Technological risks study guide* (AFF / Club Ammoniac - 1995).

[14] This characteristic, which has not yet been exploited industrially, may enable a significant reduction in the size and cost of compressors.

[15] L'ammoniac utilisé comme frigorigène, *Ammonia used as coolant* (INTERNATIONAL INSTITUTE OF REFRIGERATION I.I.R. / I.I.R - 1993).

- the relatively high pressures that it needs requiring steel thicknesses greater than those of compounds used with halogenated refrigerants.

Ammonia's ignition hazard and toxicity are dealt with in greater detail in the following paragraphs.

Implementation of ammonia[11]

Ammonia differs in its implementation in relation to halogenated fluids in the following ways:

- the design of refrigeration systems is simpler (based on the unique general behaviour of ammonia). The use of each of the halogenated fluids and their azeotropic mixtures requires complete specific knowledge of the refrigerant associated with lubrication oil problems (zero, total or partial miscibility), transport properties, and thermal exchange coefficients, etc... ,

  Furthermore, with this design, the size of return lines does not pose a problem for solving oil return problems. Only the return of liquid to the compressor must be avoided.
- the operation of an ammonia-based system can be more complicated. Ammonia systems require a set of different components and often more difficult to procure than those used for halogenated fluids,
- welders must have specific skills associated with steel pipe technology and their assembly (approved by the Institut de Soudure as per standard NF A 88-110, etc.),
- circuits must be perfectly hermetic. These guidelines are less strict in the final preparation of the circuit. Considering the water solubility of ammonia, there is no need to apply a high vacuum to the circuits prior to filling,
- for the same internal circuit volume and identical fill factor, the mass of ammonia is 2 times lower than that of halogenated fluids,

- the installations must be permanently monitored by alarm systems (explosimeters). When a leak occurs and for a given threshold, an air extraction system must come on in the machine room and the operating personnel informed. A 2nd threshold must correspond to a general alarm and the disconnection of power to the electrical circuits in the machine room[16].

The use of cold and installation typology

There are nearly 300,000 ammonia compression installations operating throughout the world [17], excluding household refrigerators and lost heat recovery industrial installations. Derived from well-controlled technology, ammonia has been used as a refrigerant for more than a century. These machines cover nearly all of our industrial or domestic needs in terms of medium or very large refrigeration capacity (greater than or equal to 100 kW of refrigeration).

Data relative to storage facilities in France [18/19]

Type of store	Number	Capacity (m^3)
Public refrigeration storage facilities	293	5,604,193
Private refrigeration storage facilities	4,984	9,456,470
Fruit packing houses	909	5,448,799
TOTAL	6,186(*)	20,509,462

(*) The profession indicates that 400 freezing companies representing 28,500 t/day of freezing are associated with some of these warehouses or cold storage facilities. More efficient for low temperatures (quick-freezing), ammonia is used in 36% of the sites although represents 55% of the installed power (S.E.I. / Profession meeting of July 27, 1993).

---

16 Détection de mélanges air/ammoniac à faible concentration / Recommandations, *Detection of air/ammonia mixtures at low concentration / Recommendations* (I.N.R.S. - 1992).

17 12 technologies pour l'avenir de l'environnement, *12 technologies for the future of the environment* (Ministère de l'Industrie et du Commerce Extérieur / SRI International - 1992).

18 L'entreposage frigorifique français en chiffres, *French cold storage in numbers* - F. BILLARD and G. PIERSON
(Magazine Générale du Froid, No. 50 - October 1992).

19 SAVE summer training program - Club M3E (Association Française du Froid /A.F.F. G. VRINAT - 1994).

Data relative to the quantities of refrigerant used

All French industries dealing with refrigeration would represent a stock of refrigerant of approximately 33,000 t [20]; 27.5% of this capacity would be used in industries associated with human food, that is nearly 9,100 t made up of C.F.C. (R12, R502), H.C.F.C. (R22 mainly) and ammonia.

Type of activity	Source	CFC (t)	HCFC (t)	NH3 (t)	Total (t)
Public refrigeration storage facilities	USNEF	60	400	540	1,000
Private refrigeration storage facilities	Estimation	102	700	900	1,702
Fruit packing houses	Estimation	60	400	500	960
Ice creams and ices	FICUR	27	40	115	182
Quick-frozen product factories	FICUR	11	70	210	291
Fresh dairy products	EDF	-	560	840	1,400
Beverages	EDF	15	25	170	210
Meat processing	EDF	-	1,000	980	1,980
Vegetable processing	EDF	-	240	720	960
Baking industry	EDF	-	150	90	240
Grain processing	EDF	100	10	75	185
Grand total (t)		375	3,595	5,140	9,110
Percentages		4	39.5	56.5	100

The table above shows that the C.F.C.s are used very little in the food industries, that H.C.F.C.s represent a large portion, to be replaced in the relatively near future, and that ammonia is already the most widely used refrigerant. A Dutch study [21] arrives at comparable results. The International Institute of Refrigeration also indicates that ammonia represents 59% of refrigerants (31% for the H.C.F.C.s with R22, 1% for the C.F.C.s with R12 and 9% with R502).

Of the 176 ice skating rinks in France, 91 are direct expansion type and 85 use a secondary refrigerant (glycol water or brine). C.F.C. 12 is used the most (400 t), while H.C.F.C. 12 represents 88 t and ammonia 43 t. In French ports, 170,000 t of ice is manufactured each year in the form of chips by direct expansion of ammonia. This activity sector represents 14 t of ammonia for the entire sector.

---

[20] "Revue des applications électriques dans le résidentiel et le tertiaire", *Review of electrical applications in the residential and tertiary sector*, No. 35 - October 1993.

[21] Ammonia as refrigerant. Applications and risks - R. J. M. VAN GERWEN (IIF B2 Hannover- May 1994).

Installations can be classified according to various criteria such as evaporation temperature, ammonia distribution system, condensation mode, number of compressor stages and of course, according to the various applications[22]. This final classification is intentionally presented last using 7 different diagrams.

Classification according to evaporation temperatures

System	Temperature (°C)	Application
T1 - Low temperature	- 40 to - 45	Quick freezing
T2 - Medium temperature	- 25 to - 30	Frozen food storage
T3 - High temperature	- 10 to 0	Refrigeration
T4 - Very high temperature	$T_0 > 10$, $T_k < 70$	High temp. heat pump

Classification according to the fluid distribution system

D1 - Electric or thermostatic expansion valve: a system that is little used in the industry, although which could have applications in liquid cooling units, heat pumps and commercial or small industrial installations (slaughterhouses).

D2 - Gravity: from LP cylinders supplied by a float expansion valve, the circulating output can be 6 to 8 times the vaporised output, the pressure is essentially the same as the evaporation pressure, the connecting lines have equivalent diameters. All of the following applications are generally located in buildings.

- Many small and medium-size coolers use finned type evaporators that are gravity fed by individual cylinders (fruit coolers, slaughterhouses).
- Freezing or cooling tunnel evaporators supplied by individual cylinders (yoghurt tunnels, fluidised beds, etc.).
- Evaporators immerged in tanks of iced water or brine supplied by overheating cylinder (dairies, ice cream manufacturers, etc.).
- Multiple-tube evaporators supplied by floater expansion valve (water coolers or glycol water for breweries, etc.).

---

22 Guide d'étude des risques technologiques, *Technological risks study guide* (AFF / Club Ammoniac - 1995).

D3 - By low pressure pump: from a supply cylinder, the liquid of which is expanded by a HP or LP floater expansion valve, the liquid output from the pump is 4 to 10 times the vaporised output and the discharge pressure is 3 to 4 bar greater than the intake pressure. The connecting lines can be long, of large diameter, and are located within the buildings. Certain sections can circulate in the open air on a framework. The applications are increasingly numerous (freezing or cooling tunnel evaporators, freezer plate cabinets, large coolers).

Classification according to condensation mode

C1 - By air:

- Air-cooled refrigerant condenser: it is installed outside except in the case of heat pumps; the condenser and the subcooler are thus integrated in the process.
- Evaporative refrigerant condenser (exterior): the tank is generally located at the liquid outlet.

C2 - By water:

- Horizontal multipipe condenser (interior or exterior).
- Vertical trickling condenser (exterior).

Classification according to the number of compression stages

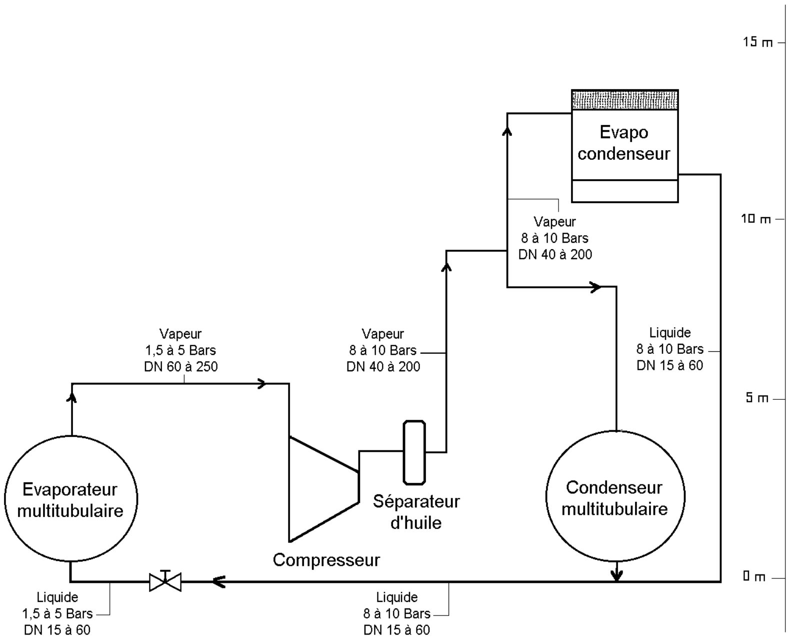
E1 - Single stage units: temperature difference (T_k - T_0) less than 50°K.

E2 - Two-stage units: temperature difference (T_k - T_0) greater than 50°K.

Classification by installation type (8 main applications)

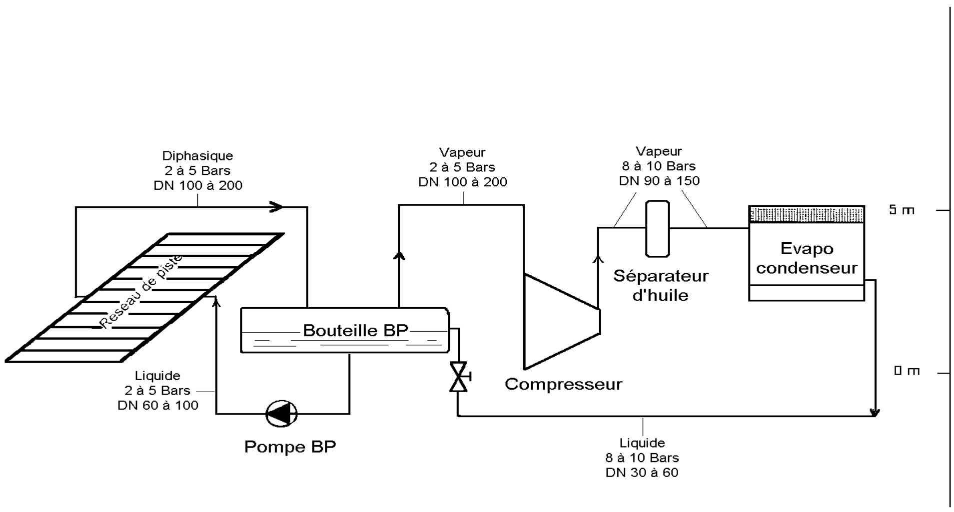
The diagrams below indicate the habitual location of the installations, the nature and most frequent arrangement of the main equipment, the size range of pipes and the possible risk(s).

A1 - Liquid cooler unit



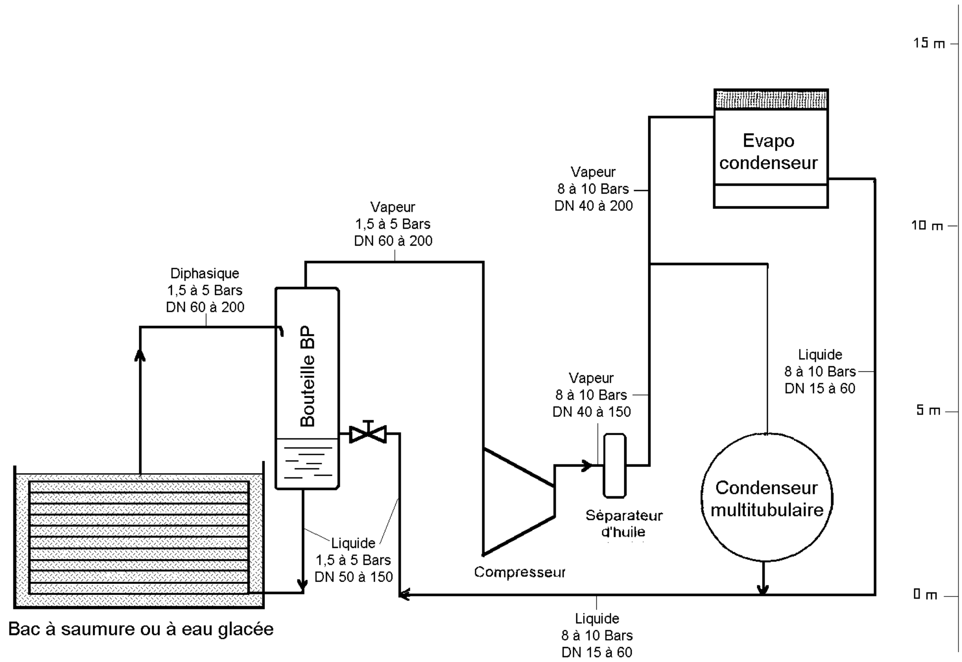
This type of installation is very widely used in all agriculture & food industries and in the air-conditioning sector.

A2 - Ice skating rink



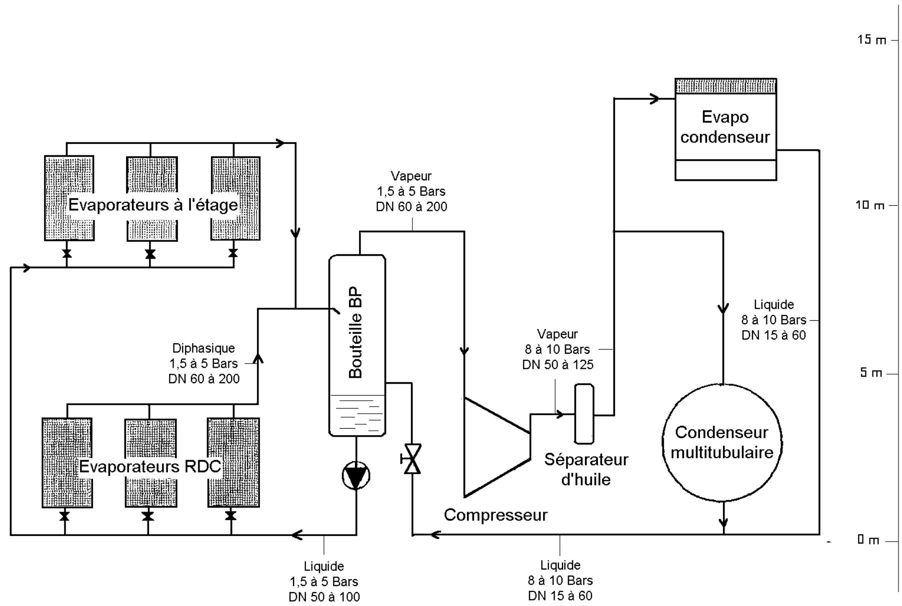
These installations form part of the rare installations where ammonia is used in a public facility. The pipe network maintaining the ice rink is embedded in a concrete slab and may extend several tens of km in length.

A3 - Brine and iced water tanks

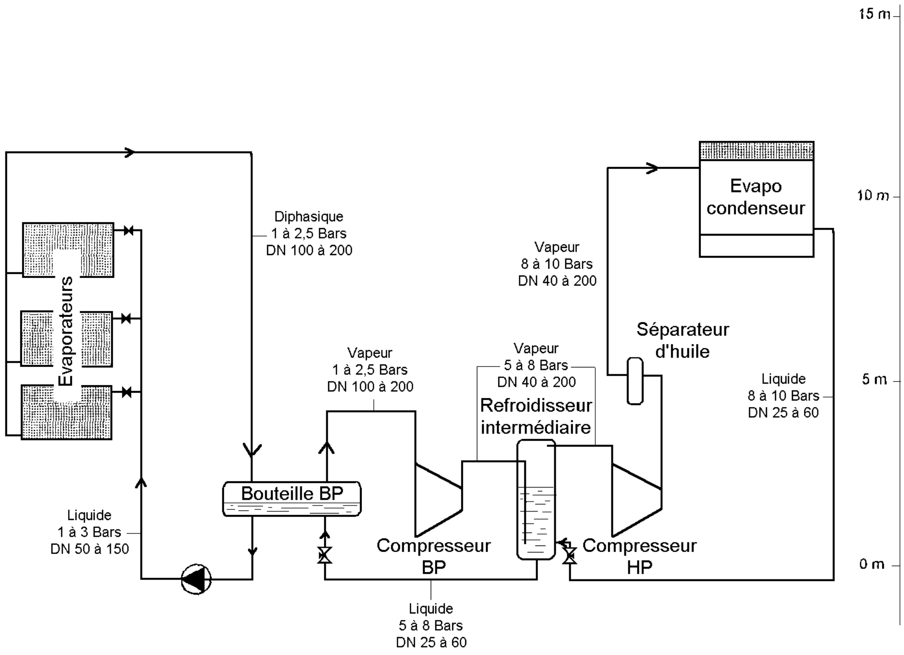


This type of installation is used in dairies and in air-conditioning facilities. The brine or iced water is an indirect cooling system.

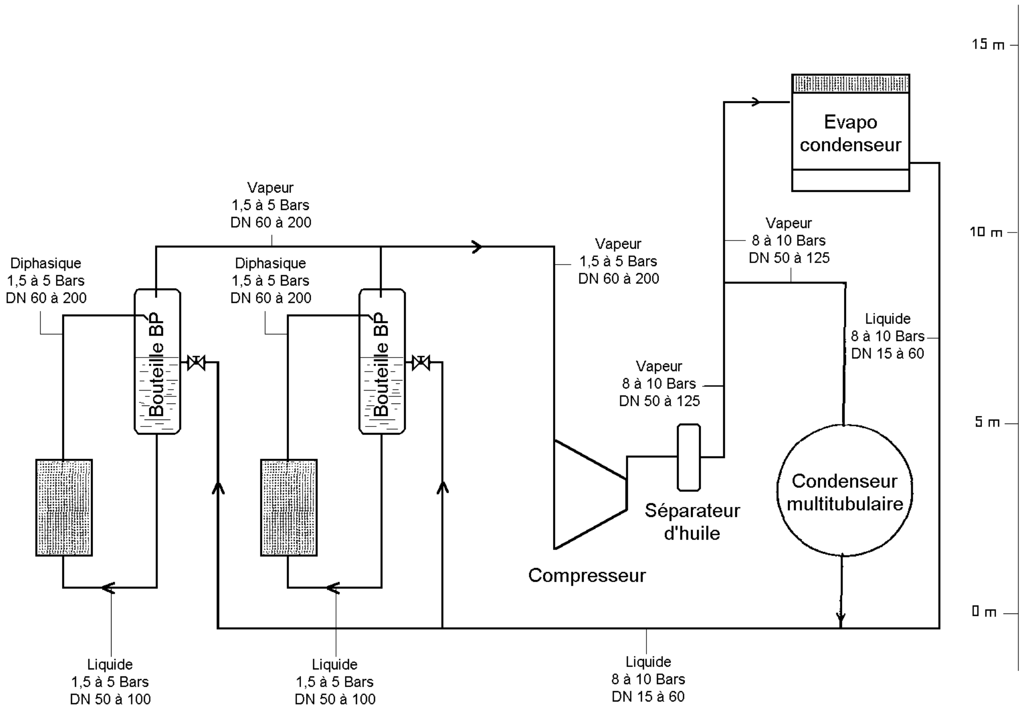
A4 -Freezing rooms and tunnels



A5 - Quick-frozen food storage

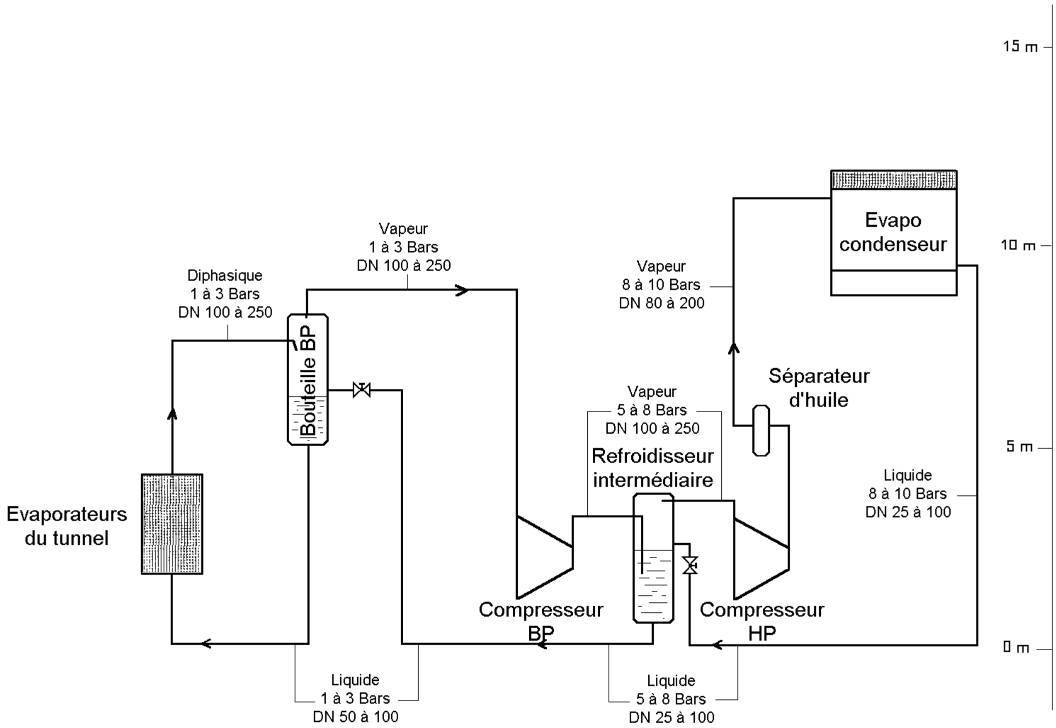


A6 - Cooling rooms



These installations are used in all agriculture & food industries.

A7 - Freezing tunnels



These installations are used in all agriculture & food industries.

An 8th group, referred to as "A8", made up of high temperature air/air heat pumps is not depicted here.

The following table includes all of the installations mentioned above while associating the various classification criteria presented.

Application	Evaporation	Distribution	Condensation	Stages
A1	T2 or T3	D2	C1 or C2	1 or 2
A2	T3	D3	C1	1
A3	T3	D2	C1 or C2	1
A4	T3	D2 or D3	C1	1
A5	T2	D3	C1	2
A6	T3	D2 or D3	C1	1
A7	T1	D2 or D3	C1	2
A8	T4	D1	C2	1 or 2

Administrative situation

Article 1 of the Act of July 19, 1976 requires facilities liable to compromise public safety and sanitation to request authorisation or declare their activities. Those concerned fall under the various headings of the list of classified industrial sites for the protection of the environment.

Refrigeration (or compression) installations operating at gauge pressures above 1 bar are thus concerned, particularly if they compress or use a flammable or toxic fluid such as liquefied ammonia.

Until July 1992, facilities were subject to either:

- authorisation, for input power greater than 300 kw (361.A.1), or
- declaration, for input power less than or equal to 300 kw (361.A.2).

Section 361 is essentially deals with sound nuisance possibly associated with the operation of the main equipment in facilities (ventilators, compressors, etc.) and not by the risks associated with the toxicity and the flammability of ammonia. In certain installations, large quantities of ammonia can be present, part of which is contained in a buffer tank with a capacity of several m^3 (confined or otherwise).

This tank can be considered as a liquid ammonia storage facility, possibly associated with a refrigeration facility, and governed in this respect by section 50.

- under the authorisation regime, when the storage facility consists of tanks (or recipients) having a unitary capacity of:
  - greater than 10 t or if the total quantity of the ammonia stocked exceeds 50 t (50.1),
  - greater than 50 kg but less than or equal to 10 t, if the total quantity of ammonia stocked is greater than 150 kg but less than or equal to 50 t (50.2),
  - less than or equal to 50 kg, if the total quantity of ammonia stocked is greater than 5 t but less than or equal to 500 t (50.3.a).
- under the declaration regime, when the storage facility consists of tanks or recipients with a unitary capacity less than or equal to 50 kg, if the total quantity of ammonia stocked is greater than 150 kg but less than or equal to 5 t (50.3.b).

With this interpretation of the nomenclature, the majority of refrigeration installations subject to declaration as per section 361 should have benefited from the authorisation regime. Dated February 20 and April 2, 1976, two documents from the SEI ("Service de l'Environnement Industriel", Service for the Industrial Environment) stipulate, respectively:

- that "all refrigerated storage facilities having liquid ammonia storage greater than 50 kg, the quantity stocked being greater than 150 kg, fall within the 2nd class of the classified installations nomenclature, independently of activities conducted jointly",
- that "an ammonia storage facility (cylinders, for example) must be properly distinguished which, owing to its size, may be classified as such, from ammonia tanks existing in the liquefied ammonia system of refrigeration equipment, which form an integral part of this installation classed in the 3rd category under the terms of section 361, and cannot be considered as a storage facility".

The Decree of July 7, 1992 modified the nomenclature by removing activity No. 50 and by creating section No. 1136 "Emploi ou stockage de l'ammoniac" (*Use and storage of ammonia*). All ambiguity has thus been removed, as the use and storage of liquefied ammonia is now governed by:

- an authorisation with public easement, if the total quantity likely to be present in the installation is greater than or equal to 500 t (1136.1),
- an authorisation, if the total quantity likely to be present in the installation is greater than 50 t, but less than 500 t (1136.2) or if the ammonia is stored in a single tank:
  - greater than 50 kg, if the total quantity likely to be present in the installation is greater than 150 kg, but less than or equal to 50 t (1136.3),
  - less than or equal to 50 kg, if the total quantity likely to be present in the installation is greater than 5 t, but less than or equal to 50 t (1136.4a),
- a declaration, if the ammonia is stored in tanks with a capacity less than or equal to 50 kg and if the total quantity likely to be present in the installation is greater than 150 kg, but less than or equal to 5 t (1136.4b).

Section 361 will be replace by section 2920 "Installations de réfrigération ou compression fonctionnant à des pressions effectives supérieures à 10^5 Pa", (*Refrigeration or compression installations operating at gauge pressures above* 10^5 *Pa*),

- compressing or using flammable or toxic fluids, the input power being greater than 300 kW (authorisation) or greater than 20 kW, but less than or equal to 300 kW (declaration),
- in all other cases, the input power being greater than 500 kW (authorisation) or greater than 50 kW, but less than or equal to 500 kW (declaration).

Nuisances and risks associated with the operation of installations

A refrigeration installation, like all other technical equipment, poses specific risks. These risks are especially related to the products used in the transfer loops to trap, transport and draw off excess calories.

Generally speaking, the heat transfer fluid may be flammable, toxic and liable to effect the ozone layer in the upper atmosphere or participate in the "greenhouse effect".

Nuisances

It should be reminded that refrigeration installations:

- generally operate in a closed system and generate few nuisances during normal operation,
- often are equipped with a cooling system using "evaporative" type refrigerant condensers possibly creating water vapour (steam) to a certain extent,
- do not produce waste, excluding any used oil,
- are equipped with potentially noisy equipment (compressor, associated cooling equipment, etc.) and must be designed or equipped to limit noise pollution as much as possible.

Potential risks

The main physical and thermodynamic characteristics of the ammonia used as a refrigerant and a Material Safety Data Sheet are presented in the appendices hereto[23].

Fire / explosion risks

Ammonia is considered as a relatively non-flammable gas[24]. Its explosive limits in air are between 15 and 28%. However, a study indicates that the L.E.L. may be reduced by 4% in presence for a cloud consisting of oil (simultaneous lubricant leak) and aerosol ammonia[25].

The self-ignition temperature of ammonia is 630°C. As it dissolves in nitrogen beginning at 450 - 550°C, the combustion obtained can result from the hydrogen formed.

---

[23] Appendices 3 and 4: physical and thermodynamic characteristics of ammonia / Material Safety Data Sheet.

[24] Material Safety Data Sheet No. 16 (I.N.R.S.)

[25] A.F.F. Seminar / International Institute of Ammonia Refrigeration (U.S.A.).

Although much greater than the majority of hydrocarbons, its minimal ignition energy (680 mJ) is nevertheless less than that delivered by a switch spark (1 J).

Ammonia's flammable and explosive character, particularly in a confined space, is a subject of controversy. A bibliography compiled in 1991 [26] stipulates that all the flammability and explosivity characteristics published indicate that ammonia is a combustible gas which is quite less reactive, vis-à-vis air, than the majority of other combustible gas, and methane in particular. As such, the minimum ignition energy of an air / ammonia mixture is greater, the flame in the mixture propagates with more difficulty and slower; the violence of the explosion is weaker in a closed recipient. The study sites a few accidents abroad in which ignition/explosion of ammonia is suspected. A summary of the accidents concerned is provided in the appendix hereto[27].

Given the current level of understanding and without precise elements about these accidents (no known case is recorded in France), this risk is touched upon only lightly in this study. The same is not true, however, for fires associated with the environment in the vicinity of the installation (numerous cases are known particularly as a result of the insulation materials used), the latter possibly being the cause of a possible domino effect.

Toxic hazard

With the exception of air, rarely used in these conditions, all refrigerants are potentially harmful to man when their concentration in the air reaches a certain level. Fatal accidents resulting from anoxia have even been encountered with C.F.C.s. However, ammonia is one of the refrigerants whose toxicity is a dominant characteristic. The explosion of a 22-ton tank of ammonia in Dakar, Senegal on March 24, 1992 (129 dead and more than 1,100 injured) reminds us that the toxicity of this product can also result in a "delayed effect" which is responsible for numerous deaths even weeks after an accident.

Normally confined in the recipients and pipes of a refrigeration system, ammonia can be released to the open air in an accidental situation, especially resulting from:

- normal operation of safety devices (valves, blow-out discs),
- operational failure (a poorly-controlled purge of a circuit, etc.),

[26] Etude bibliographique - Caractéristiques d'inflammabilité et d'explosivité de l'ammoniac, *Bibliographical study - Inflammability and explosivity characteristics of ammonia* (INERIS / Mr. PINEAU/ Mrs. ABIVEN/ Mr. CHAINEAUX - October 1991).

[27] Appendix 7: list of known accidents since 1968 (France / World).

- through a limited leak (seal, loss of seal on a valve, corrosion, etc.),
- after equipment rupture (explosion caused by a fire, impact or equipment failure, etc.).

The ammonia released may then form a toxic cloud in the atmosphere and possibly cause water pollution if a permanent flow of water is located nearby (wastewater/rainwater collector, etc.) or following inappropriate maintenance or servicing (sprayed water from a curtain not collected, etc.).

- A limited leak corresponds to a continuous liquid or gaseous phase release and at a constant or nearly constant rate. Its duration depends on the technical characteristics of the installation, the location of the "break", and the emergency response resources and the intervention time.
- The rupture instantly releases a significant quantity or all of the ammonia essentially in the form of an initial flash (up to 20% of the mass of NH_3 released for an ambient temperature of 25°C), generally followed by a second release corresponding to the slow vaporisation of the residual liquid product released.

ACCIDENT ANALYSIS

This study essentially concerns refrigeration installations using ammonia as refrigerant. However, in order to better understand and to place the risks associated with these installations in perspective, quantified information has also been collected on numerous accidents, both French or foreign, in other industrial or agricultural activities and in the field of transport. The processing of these data allows a number of comparisons to be made using general indicators (geographic distribution, nature, accident causes and consequences, etc.).

Furthermore, while the nature and significance of the hazards presented are particularly different, the case studies bring into play liquid, gaseous ammonia or its aqueous solutions. These various phases can be presented for a given activity or during an accident (normal physical state of the product, transfer of risks or pollution during an intervention in a normal or accidental situation, etc.). Excluding special cases that are especially associated with the type and the consequences of certain accidents, the ammoniacal solutions used as liquid fertilizers are not taken into account however.

The sample studied consists of:

- 91 French refrigeration accidents (January 1980 to December 1994),
- 44 foreign refrigeration accidents (January 1958 to December 1992),
- 71 French accidents excluding refrigeration (August 1968 to December 1994),
- 150 foreign accidents excluding refrigeration (July 1959 to May 1994).

The first approach is then completed by a detailed presentation of a few representative and particularly significant accidents in terms of feedback (cause of the accident, sequence of events, consequences, etc.).

Nature and characteristics of the sample studied

A biographical study and a query of the ARIA database enabled us to identify 356 accidents, from July 1959 to December 1994, involving ammonia and/or its aqueous solutions. The compiled sample is very diverse owing to the diversity of the sources of information, the kind and size of the events, as well as the more or less high level of detail of the information gathered.

The following table thus shows that 14% to 32% of the accidents studied generally lack information (origin of the toxic leaks, possible release of ammonia during a fire or following an explosion, consequences of the accident, etc.).

General information	France (162)					Abroad (194)				
	R[28] (91)		not R[29] (71)		TOT.	R (44)		not R (150)		TOT.
	Nb[30]	%	Nb	%	%	Nb	%	Nb	%	%
Few/no accidents reported	28	**30.8**	10	**14.1**	23.5	12	**27.3**	52	**31.8**	33.0
Fire /explosion (NH_3 leak?)	23	**25.3**	1	**1.4**	14.8	2	**4.6**	9	**6.0**	5.7
Origin of leak not specified	13	**14.3**	8	**11.3**	13.0	15	**34.1**	39	**26.0**	27.8

Considering the various elements mentioned above, the use of this population for comparison purposes must be undertaken with care. The term "aggregate indicators" is thus used rather than "statistics". In order to ensure a minimum amount of consistency in the analysis presented below, the French and foreign accidents as well as the accidents concerned are systematically differentiated.

Consequently, the accidents studied are split according to the following 4 criteria:

- **French / foreign / related** or **not related** to a refrigeration installation.

A short presentation of the accidents in the field of refrigeration is enclosed at the end of this document[31].

[28] Refrigeration installations

[29] Other installations (excluding refrigeration).

[30] Number of known accidents.

[31] Appendix 7: list of known refrigeration accidents since 1958 (France / World).

Stakes and key figures

Of all the accidents studied, 54.5% occurred abroad and 45.5 % in France. Refrigeration installations represent 56.2% of the accidents in France and 22.7% of the accidents abroad.

The following tables present a distribution of the activities concerned, the typology of the accidents and their origins and consequences (an accident may correspond to several items).

Annual distribution

In this distribution of the accidents studied and the human consequences, the victims among the employees, rescue personnel and the public are not distinguished.

Year	France (162 cases)								Abroad (194 cases)							
	R (91 cases)				not R (71 cases)				R (44 cases)				not R (150 cases)			
	A	**D**	**I**	**E/C**	**A**	**D**	**I**	**E/C**	**A**	**D**	**I**	**E/C**	**A**	**D**	**I**	**E/C**
< 1980	**-**	-	-	-	**3**	6	>27	?	**16**	14	270	-	**64**	98	1800	>22300
1980/86	**13**	-	1	-	**11**	2	16	?	**9**	14	166	>4100	**48**	30	>1400	>27000
1987	**3**	-	1	-	**3**	-	-	?	**3**	12	50	200000	**6**	10	72	21000
1988	**5**	1	2	30	**10**	-	54	-	**3**	-	-	-	**8**	2	26	>1220
1989	**7**	-	-	>28	**9**	-	3	>900	**5**	1	1700	9100	**12**	11	680	>52400
1990	**12**	-	7	>600	**9**	-	12	?	**-**	-	-	-	**4**	3	>400	>7000
1991	**8**	-	5	>35	**4**	-	1	22	**2**	-	6	-	**4**	17	150	>500
1992	**12**	-	7	?	**5**	-	4	700	**6**	1	9	?	**2**	129	1150	-
1993	**10**	-	42	?	**8**	-	19	-	**-**	-	-	-	**1**	-	9	-
1994	**21**	-	122	>500	**9**	2	4	>20	**-**	-	-	-	**1**	-	?	-
TOTAL	**91**	1	187	>1200	**71**	10	>140	>1700	**44**	42	>2200	>210000	**150**	300	>5600	>131000

A: number of accidents **D:** number of deaths **I** number of injured / intoxicated
E/C: number of people evacuated / confined

The consequences of accidents abroad are generally more severe (victims, etc.) and are most often known as a result of widespread international coverage (notification, press, etc.).

Of the population studied in France, refrigeration installations are responsible for 50 to 70% of known accidents and potentially involving ammonia or its aqueous solutions. Undoubtedly, numerous other cases are not declared, particularly those that occur in small installations. A single accident resulted in the death of one person while there were 10 victims in accidents that were not refrigeration-related. This proportion (approx. 1/10) is appreciably less than that calculated based on foreign accidents (1/2).

The number of deaths/accident ratios are as follows:

Country	Refrigeration related	Not refrigeration related
France	0.01	0.14
Abroad	0.95	2.00

The people that were injured, effected or more or less intoxicated by the ammonia cloud are most generally employees or rescue personnel, and rarely the general public.

In France, confinement or evacuation is most often limited to the employees at the site where the accident occurred.

Monthly distribution of accidents according to the days of the week (French accidents)

The following two tables provide the distribution of French refrigeration-related accidents according to the month of the year and the days of the week. The foreign accidents that are excessively varied in space and time are not treated.

Month	R (91 cases)		not R (71 cases)	
	Nb	%	Nb	%
January	5	5.5	1	1.4
February	2	2.2	5	7.0
March	7	7.7	8	11.3
April	3	3.3	5	7.0
May	3	3.3	6	8.5
June	11	12.1	11	15.5
July	6	6.6	2	2.8
August	17	18.7	5	7.0
September	13	14.3	7	9.9
October	12	13.2	10	14.1
November	7	7.7	3	4.2
December	5	5.5	8	11.3

Day	R (91 cases)		not R (71 cases)	
	Nb	%	Nb	%
Monday	15	16.5	9	12.5
Tuesday	11	12.1	8	11.1
Wednesday	12	13.2	8	11.1
Thursday	19	20.9	17	23.6
Friday	18	19.8	13	18.1
Saturday	10	11.0	11	15.3
Sunday	6	6.6	5	6.9

There are generally more accidents in June and during the months of August, September and October. The available information rarely indicates the exact circumstances, although the periods observed correspond to annual holiday periods (fewer people at work), seasonal operation stoppages (shut-down/restarting of installations) and large outdoor job sites (refurbishing of abandoned sites, etc...). The intensive use of equipment associated with hot summer temperatures may also be considered for the refrigeration installations.

In the sample studied, both refrigeration-related and non refrigeration-related accidents occur most often on Thursdays and Fridays. For the refrigeration-related accidents, the start of the week is also a sensitive period compared to other activities where numerous cases are recorded on Saturday (continuous production operations, etc...).

Regional distribution

The following table presents the region distribution (France) of the accidents studied.

Region	Refrig. (91)		Not refrig. (71)		Total (162 cases)	
	Nb	%	Nb	%	Nb	%
Alsace	5	5.5	3	4.2	8	4.9
Aquitaine	8	8.8	8	11.3	16	9.9
Auvergne	4	4.4	-	-	4	2.5
Basse Normandie	6	6.6	1	1.4	7	4.3
Burgundy	3	3.3	5	7.0	8	4.9
Brittany	16	17.6	3	4.2	19	11.7
Centre	-	-	3	4.2	3	1.9
Champagne Ardenne	4	4.4	4	5.6	8	4.9
Franche Comté	1	1.1	1	1.4	2	1.2
Haute Normandie	1	1.1	5	7.0	6	3.7
Ile de France	1	1.1	3	4.2	4	2.5
Languedoc Roussillon	2	2.2	-	-	2	1.2
Lorraine	10	11.0	3	4.2	13	8.0
Midi Pyrénées	-	-	1	1.4	1	0.6
Nord Pas de Calais	3	3.3	14	19.7	17	10.5
Pays de la Loire	8	8.8	2	2.8	10	6.2
Picardy	4	4.4	2	2.8	6	3.7
Poitou Charentes	1	1.1	-	-	1	0.6
Provence Alpes Côte d'Azur	3	3.3	3	4.2	6	3.7
Rhône Alpes	11	12.1	10	14.1	21	13.0

Five regions (Aquitaine, Brittany, Lorraine, Nord-Pas-de-Calais and Rhône-Alpes), each with between 8 and 13% of the accidents, concentrate 53% of the cases listed.

For the Aquitaine and Rhône-Alpes regions, the distribution between refrigeration-related activities and the other activities is balanced (50%). It can be noted, however, that:

- Brittany and its significant agriculture & food activity (animal husbandry, slaughterhouses, etc.) represent 18% of refrigeration-related accidents (4% for the other installations),
- the Nord-Pas-de-Calais with its heavy industry especially associated with ammonia derivatives (fertilizer, etc.) represents 20% of non refrigeration-related accidents (3% for refrigeration installations),
- certain regions are particularly concerned by accidents related to the agricultural use of ammonia for soil management purposes (Champagne-Ardennes, etc.).

These regions are also ranked number one in terms of the overall capacity of their perishable foodstuff storage facilities, including Brittany with 2,357,107 m^3 (production region), Rhône-Alpes with 1,430,940 m^3 and Nord with 1,272,401 m^3 (consumption regions). This is also true for Pays-de-la-Loire (1,211,100 m^3) or Aquitaine (701,742 m^3) which have a large volume of fruit packinghouses. Ile-de-France, however, with 1,684,735 m^3, does not stand out in terms of the number of accidents[32].

Distribution by activity

The lack of homogeneity of the information collected must be mentioned again, especially concerning the foreign accidents. The databases generally mention only the most significant events; the kind of accident, its origin and the activity at issue are not always indicated. In addition, the sample studied only includes a limited number of accidents (356 cases).

Concerning the accidents and of the 745 ammonia-related incidents between 1977 and 1979, the "California Department of Industrial Relations, Division of Labour Statistics on Research" gives the following distribution[33]:

• factories	28.2%	• agriculture	11.1%	• transports	3.5%
• misc.	18.5%	• services	11.1%	• construction	2.8%
• retailers	16.0%	• wholesalers	8.6%	• mining	0.1%

32 L'entreposage frigorifique français en chiffres, *French cold storage in numbers* - F. BILLIARD & G. PIERSON - October 1992).

33 Eléments de sûreté chimique et de désastrologie, *Elements of chemical safety and disasterology* (C.E.A. / D.A.S. - M. ANDURAND - December 1989).

The "U.S. Department of Transport" reported 585 incidents which took place during transports and which resulted in the release of ammonia between 1971 and May 1980[32]:

- Railroad 73.7%
- Miscellaneous 2.2%
- Air 0.3%
- Road 23.6%
- Water 0.2%

Considering the reservations indicated above, the tables on the following two pages give an approximate distribution of accidents by activity, classified according to the French professional activity code (N.A.F), for the entire sample studied. It should be noted that a distribution of the number of establishments by activity and by number of salaried employees, in France and for the main activities concerned, is enclosed in the appendix hereto[34].

a) Refrigeration systems

Activity (135 cases studied)	France (91 cases)		Abroad (44 cases)	
	Nb	%	Nb	%
01 - Agriculture, hunting & auxiliary services	**5**	**5,5**	-	-
including 01.1 - Crops	1	1.1	-	-
01.3 - Crops & associated animal farming	1	1.1	-	-
01.4 - Services related to agriculture (cooperatives)	3	3.3	-	-
05 - Fishing, aquaculture	**1**	**1.1**	**4**	**9.1**
15 - Food industries	**58**	**63.8**	**24**	**54.7**
including 15.1 - Meat processing industry	28	30.8	2	4.6
15.2 - Fish industry	-	-	1	2.3
15.3 - Fruit and vegetable industry	5	5.5	-	-
15.5 - Dairy industry	13	14.3	7	15.9
15.7 - Fabrication of animal feed	1	1.1	-	-
15.8 - Other food industries	8	8.8	9	20.5
15.9 - Beverage industry	3	3.3	3	6.8
**.* - Undetermined	-	-	2	4.6
24 - Chemical industry	**4**	**4.4**	**3**	**6.8**
including 24.1 - Basic chemical industry	4	4.4	3	6.8
25 - Rubber and plastics industry	**2**	**2.2**	-	-
including 25.2 - Transformation of plastic materials	2	2.2	-	-
29 - Fabrication of machines and equipment	**1**	**1.1**	-	-
including 29.2 - Fabrication of general purpose machines	1	1.1	-	-
50 - Automotive merchandising and repair	**1**	**1.1**	-	-
including 50.2 - Maintenance & repair of automobiles	1	1.1	-	-
51 - Wholesale & intermediate trade	**5**	**5.5**	-	-
including 51.1 - Wholesale intermediaries	1	1.1	-	-
51.3 - Wholesale of food products	4	4.4	-	-
63 - Transport auxiliary services	**10**	**11.0**	**9**	**20.5**
including 63.1 - Handling and storage	10	11.0	9	20.5
92 - Recreation, cultural & sport activities	**4**	**4.4**	-	-
including 92.6 - Sport-related activities (ice skating rinks)	4	4.4	-	-
YY - Activity undetermined	**-**	**-**	**4**	**9.1**

While the activities are not determined for 9% of foreign accidents, a distribution by sectional branch of the case studies leads to results of the same magnitude in France or abroad.

---

34 Appendix 5: nombre d'établissements en France pour les principales activités concernées, *number of establishments in France for the main activities concerned* (extract from I.N.S.E.E. - 1992).

Refrigeration installations directly associated with agricultural & food activities and the storage of foodstuffs (N.A.F. codes 01, 15, 51 and 63) are responsible for 86% of the accidents in France (75% abroad).

Numerous accidents occur in small production units (slaughterhouses, meat packing plants, etc.). Excluding agricultural cooperatives, the "manufacturing activities" (milk and meat, in particular) and their associated storage facilities, represent 64% of the accidents in France (55% abroad). Industrial storage facilities (N.A.F. codes 51 and 63) take 2nd place with 17% of the cases in France (21% abroad).

b) Miscellaneous activities (Not refrigerating installations)

Activity (221 cases studied)	France (71 cases)		Abroad (150 cases)	
	Nb cases	%	Nb cases	%
01 - Agriculture, hunting & auxiliary services	**14**	**19.7**	-	-
including 01.1 - Crops	4	5.6	-	-
01.3 - Crops & associated animal farming	8	11.3	-	-
01.4 - Services related to agriculture (cooperatives)	2	2.8	-	-
05 - Fishing, aquaculture	**1**	**1.4**	**-**	**-**
14 - Other resources industries	**1**	**1.4**	**-**	**-**
including 14.2 - Extraction of sands and clays	1	1.4	-	-
15 - Food industries	**-**	**-**	**1**	**0.7**
including 15.4 - Industry of fats and oils	-	-	1	0.7
21 - Paper and cardboard industry	**1**	**1.4**	**-**	**-**
24 - Chemical industry	**24**	**33.8**	**59**	**39.4**
including 24.1 - Basic chemical industry	19	26.8	55	36.7
24.4 - Pharmaceutical industry	3	4.2	1	0.7
24.6 - Fabrication of other chemical products	1	1.4	1	0.7
24.7 - Fabrication of artificial / synthetic fibres	1	1.4	-	-
**.* - Undetermined	-	-	2	1.3
27 - Metallurgy	**-**	**-**	**1**	**0.7**
including27.1 - Iron and steel industry (CECA)	-	-	1	0.7
28 - Metalworking	**3**	**4.2**	**1**	**0.7**
including 28.3 - Boilerwork	1	1.4	-	-
28.4 - Forging, punching, stamping & metallurgy of powders	1	1.4	-	-
28.5 - Metal processing, general engineering	1	1.4	-	-
28.7 - Fabrication of other metal structures	-	-	1	0.7
35 - Fabrication of other transport equipment	**1**	**1.4**	-	-
including 35.2 - Construction of railroad rolling stock	1	1.4	-	-
37 - Recovery	**1**	**1.4**	-	-
51 - Wholesale & intermediate trade	**3**	**4.2**	**3**	**2.0**
including 51.1 - Wholesale intermediaries	-	-	2	1.3
51.2 - Wholesale of raw agricultural products	1	1.4	-	-
51.5 - Wholesale of non-agricultural intermediate products	2	2.8	1	0.7
52 - Retailing and repair of household items	**1**	**1.4**	**1**	**0.7**
60 - Land transportation	**14**	**19.8**	**42**	**28.4**
including 60.1 - Railroad transports	7	9.9	24	16.0
60.2 - Urban and road transports	7	9.9	9	6.0
60.3 - Pipeline transportation	-	-	7	4.7
**.* - Undetermined			2	1.3
61 - Water transport	**-**	**-**	**5**	**3.4**
including 61.1 Maritime and coastal transports	-	-	3	2.0
61.2 - Inland waterway transports	-	-	2	1.3
63 - Transport auxiliary services	**-**	**-**	**5**	**3.3**
including 63.1 - Handling and storage	-	-	5	3.3
90 - Sanitation, roadwork and waste management	**1**	**1.4**	-	-
YY - Activity undetermined	**3**	**4.2**	**30**	**20.0**
ZZ - Origin unknown	**3**	**4.2**	**2**	**1.3**

The activities or the origin of the accidents are not known in 8% of the cases in France (21% abroad).

The chemical industry is responsible for 34% of the accidents in France (39% abroad); transports take 2nd place with 20% of the cases (28% abroad). The use of ammonia in agriculture for soil amendment is also a significant source of accidents in France (20%).

Approximate distribution by accident type

The dangerous release of product (due to the toxicity of ammonia), associated with a loss of containment, is not restricted to a specific activity. In France, 73% of refrigeration-related accidents and 87% of the cases not related to refrigeration lead to the release of ammonia (liquid or gas) (98 and 91% respectively, abroad).

Releases to the atmosphere represent 52% (refrigeration-related) to 68% (not refrigeration related) of French accidents. Considering the extent of the accidents declared and the proven or potential consequences for man and his environment, this release is mentioned in more than 90% of foreign cases, while the pollution of surface water, land and underground water by ammonia solutions are rarely mentioned.

For 26% of French refrigeration-related accidents, the release of liquid ammonia (or gaseous ammonia) into the environment is not specified. The corresponding cases essentially involve a fire. This release, however, can be strongly suspected considering the extent of some of the accidents and the damage to the installations.

The following two tables present a detailed typology of the accidents studied. The comments only mention that the main specificities of the accidents recorded on the refrigeration installations or other facilities implementing ammonia.

a) Refrigeration systems

Type of accident (135 cases)	France (91 cases)		Abroad (44 cases)	
	Nb cases	%	Nb cases	%
Dangerous releases (NH_3/ NH_4OH)	**66**	**72.5**	**43**	**97.7**
➔ Into the air	47	51.6	41	93.2
➔ Into water (or sewer)	16	17.6	2	4.5
Release of NH_3/ NH_4OH not specified	**24**	**26.4**	**2**	**4.5**
N/A (no leak observed)	**5**	**5.5**	**-**	**-**
Fires	**29**	**33.8**	**15**	**34.1**
Explosions	**2**	**2.2**	**21**	**47.7**
Projections, falling equipment	**2**	**2.2**	**-**	**-**
Near accidents	**1**	**1.1**	**-**	**-**
Domino effects	**7**	**7.7**	**4**	**9.1**

Fires represent 34% of the accidents associated with refrigeration installations in France or abroad, which is 2 to 4 times more than for activities that are not refrigeration-related. A domino effect (explosion, toxic leak, etc.) was reported in 8 to 9% of the cases.

Although the information available is often imprecise, 48% of foreign accidents mention an explosion, following a fire or not. In France, this typology is reported only in 2% of the cases.

The "potential ammonia explosions" occur in a confined space and, most often, during work or rescue operations (materials-handling equipment, etc.). The presence of other chemical products (hydrogen, methane) is sometimes suspected.

b) Miscellaneous activities (excluding refrigerating installations)

Type of accident (221 cases)	France (71 cases)		Abroad (150 cases)	
	Nb cases	**%**	**Nb cases**	**%**
Dangerous releases (NH_3 or NH_4OH)	**62**	**87.3**	**137**	**91.3**
➔ Into the air	48	67.6	136	90.7
➔ Into water (or sewer)	17	23.9	6	4.0
➔ In a retaining system or onto ground only	**4**	**5.6**	**-**	**-**
Release of NH_3 or NH_4OH not specified	**1**	**1.4**	**8**	**5.3**
N/A (no leak observed)	**7**	**9.9**	**2**	**1.3**
Fires	**6**	**8.5**	**23**	**15.3**
Explosions	**2**	**2.8**	**52**	**34.7**
Projections, falling equipment	**2**	**2.8**	**9**	**6.0**
Compounded chronic pollution	**1**	**1.4**	**-**	**-**
Near accidents	**2**	**2.8**	**-**	**-**
Domino effects	**2**	**2.8**	**12**	**8.0**

Fires represent 9% of the accidents in France (15% abroad). As for refrigeration installations, 35% of the foreign cases studied lead to an explosion and 8% lead to a domino effect. These proportions are distinctly less in France (3%).

Distribution by type of consequences

Here, this distribution is also approximate. Little or no detail is provided concerning the consequences (14 to 35% of the cases reported according to the origin of the information and the kind of activity at issue). The seriousness of foreign accidents (victims, property damage, etc.) is again highlighted.

The individuals who are killed or injured at an installation are generally employees or rescue personnel. The public is involved only exceptionally. The injuries taken into account traumatic lesions as well as slight or serious intoxications. Confinement or evacuation is generally limited to the employees of the site where the accident occurred.

a) Refrigeration systems

Consequences (135 cases)	France (91 cases)		Abroad (44 cases)	
	Nb cases	**%**	**Nb cases**	**%**
Little or no accidents reported	**28**	**30.8**	**12**	**27.3**
Deaths	1	**1.1**	6	**13.6**
Seriously injured	5	**5.5**	1	**2.3**
Total injured / intoxicated	23	**25.3**	18	**40.9**
Internal property damage	41	**45.1**	32	**72.7**
External property damage	4	**4.4**	2	**4.6**
Technical unemployment	9	**9.9**	-	**-**
Shut-down of water distribution	1	**1.1**	-	**-**
Shut-down of electrical distribution	1	**1.1**	-	**-**
Evac. of people (employees/outside individuals)	19	**20.9**	7	**15.9**
Confinement of people	2	**2.2**	2	**4.6**
Limitation of traffic flow	7	**7.7**	-	**-**
Other loss of use	1	**1.1**		
Proven atmospheric pollution (complaints, etc.)	23	**25.3**	7	**15.9**
Pollution of surface water	12	**13.2**	-	**-**
Soil contamination	1	**1.1**		
Damage to wildlife	12	**13.2**	-	**-**
Damage to crops	1	**1.1**	-	**-**
Increase of risk	45	**49.5**	25	**56.8**
Other (releases to sewers, in stations, etc.)	2	**2.2**	2	**4.6**
No consequence	7	**7.7**	2	**4.6**
Unknown	3	**3.3**	2	**4.6**

In France, there has been only one accident resulting in the loss of life. The victim was a sailor who died August 25, 1988 as a result of an ammonia leak in the hold of a tuna boat in port (accident No. 393 [35]). Six accidents are known abroad (14%). There are more cases excluding refrigeration-related activities (7% in France, 25% abroad). All activities combined, the number of "injured" is of the same magnitude with 25 to 31% of the cases in France and 41 to 51% abroad.

In France, people were evacuated in 21% of the cases (16% abroad). Confinement is mentioned in only 2% of French cases (5% abroad).

Internal property damage, especially associated with a fire, is reported in 45% of the accidents in France (73% abroad). Such accidents result in technical unemployment in 10% of the cases. External damage is globally reported in 4 to 5 % of the cases. The same is true for activities that are not refrigeration-related (6%).

In 26% of French accidents, the information collected does not always indicate that a release of gaseous or liquid ammonia occurred. In France, the release of toxic products into the air (52%) is enough to create proven atmospheric pollution (complaints, etc.) in 25% of the cases studied. Abroad, these proportions are 93% and 16% respectively. Proven pollution of surface waters by the release of ammoniated solution (18% of the accidents are caused by the rinsing of a circuit, effluents produced by water curtains, dilution water, etc.) is reported in 13% of the cases. This pollution systematically results in the partial or total destruction of piscifauna.

Aggravation of the risk is systematically noted in nearly every other accident (50% in France, 57% abroad). This notion essentially takes into account the potential for explosion of ammonia tanks that are engulfed in a fire. On the contrary, 8% of French accidents had no notable consequence in terms of human, property and environmental damage (5% abroad).

---

35 Appendix 7: list 1 - Refrigeration installations / 91 French cases (1980 - 1994).

b) Miscellaneous activities (excluding refrigeration installations)

Consequences	**France (71 cases)**		**Abroad (150 cases)**	
(221 cases)	**Nb cases**	**%**	**Nb cases**	**%**
Little or no accidents reported	**10**	**14.1**	**52**	**34.7**
Deaths	5	**7.0**	37	**24.7**
Seriously injured	5	**7.0**	11	**7.3**
Total injured / intoxicated	22	**31.0**	76	**50.7**
Internal property damage	16	**22.5**	89	**59.3**
External property damage	4	**5.6**	9	**6.0**
Evac. of people (employees/outside individuals)	6	**8.5**	45	**30.0**
Confinement of people	7	**9.9**	1	**0.7**
Limitation of traffic flow	10	**14.1**	4	**2.7**
Proven atmospheric pollution (complaints, etc.)	28	**39.4**	51	**34.0**
Pollution of surface water	13	**18.3**	3	**2.0**
Pollution of underground water	-	**-**	1	**0.7**
Soil contamination	7	**9.9**	7	**4.7**
Damage to wildlife	8	**11.3**	4	**2.7**
Damage to plant life	4	**5.6**	3	**2.0**
Damage to crops	3	**4.2**	2	**1.3**
Damage to farm animals	4	**5.6**	-	**-**
Increase of risk	20	**28.2**	28	**18.7**
Other (releases to sewers, in stations, etc.)	2	**2.8**	1	**0.7**
No consequence	9	**12.7**	1	**0.7**
Unknown	1	**1.4**	13	**8.7**

In non refrigeration-related accidents, the consequences are generally more serious. People were killed in 7% of French accidents (25% abroad). In France, injured, intoxicated or effected individuals were reported in 31% of the accidents (51% abroad). Here again, the people involved essentially include employees or rescue personnel. Lesions or serious intoxication are observed in 7% of the cases (this rate is comparable to that seen in the refrigeration-related accidents: 6% in France and 2% abroad).

People were evacuated in 9% of the cases in France, most often concerning the employees, and in 30% of the cases abroad. This high number is generally associated with the significant amount of gaseous ammonia involved. Confinement is mentioned in 10% of the cases in France (less than 1% abroad).

Property damage within the establishment is reported in 23% of the accidents in France (59% abroad). External damage is reported in 6% of the cases, which is comparable to that observed in non refrigeration-related installations (4 to 6%).

In France, the release of toxic products is sufficient to lead to proven atmospheric pollution in 39% of the cases studied (34% abroad). Surface water pollution (rinsing of a circuit, effluents produced by water curtains, dilution water, etc.) is reported in 18% of the cases. Soil is polluted in 10% of the cases.

Pollution causes the total or partial destruction of aquatic fauna in 11% of accidents (this rate is comparable to that noted with refrigeration installations). Domestic animals are effected in 6% of the accidents and crops are damaged in 4% of the cases.

The risk is aggravated in 28% of French cases (19% abroad), although 13% of the accidents had no significant consequence for man or property in France.

Circumstances, nature and main origins of the accidents studied

The following tables present a summary of circumstances, the nature and main origins of the accidents studied as well as the quantity of gaseous ammonia released.

a) Accident circumstances

Circumstances	France (162)				Abroad (194)			
	R (91)		not R related (71)		R (44)		not R related (150)	
	Nb	%	Nb	%	Nb	%	Nb	%
Installation condition not known	39	**42.9**	5	**7.0**	36	**81.8**	92	**61.3**
Installation in normal operation	25	**27.5**	27	**38.0**	1	**2.3**	36	**24.0**
Installation shut-down	12	**13.2**	8	**11.3**	1	**2.3**	4	**2.7**
Installation shut-down / restart	2	**2.2**	1	**1.4**	3	**6.8**	3	**2.0**
Equipment unused / shut-down and not purged	9	**9.9**	4	**5.6**	-	**-**	2	**1.3**
Leak during or after modification / testing / maintenance / cleaning / works	15	**16.5**	11	**15.5**	3	**6.8**	7	**4.7**
Overpressure / overfilling	10	**11.0**	8	**11.3**	12	**27.3**	16	**10.7**
Normal valve / disc operation	3	**3.3**	7	**9.9**	4	**9.1**	1	**0.7**
Filling / unloading of tanks	6	**6.6**	12	**16.9**	1	**2.3**	20	**13.3**
Collision / derailing / spillage (transport)	-	**-**	10	**14.1**	-	**-**	22	**14.7**
Accident outside of the establishment	-	**-**	4	**5.6**	1	**2.3**	1	**0.7**
Wastes	1	**1.1**	6	**8.5**	-	**-**	-	**-**
Accident during intervention (works / rescue services)	12	**13.2**	4	**5.6**	5	**11.4**	5	**3.3**
→ including rescue operations	2	**2.2**	4	**5.6**	2	**4.6**	-	**-**

In France, all activities combined, the accidents occur after a modification of the installations or during maintenance operations in 16% to 17% of the cases. The installations have been shutdown, often for an extended period of time, in 11% to 13% of the cases or are out-of-service and abandoned without being purged (6% to 10%).

When refrigeration-related, the accident occurred during work or within the scope of maintenance operations in 11% of the cases .

In 11% of the cases, the origin of product leaks is related to excess pressure (fire, etc.) or overfilling (27% abroad). Gaseous ammonia releases are associated with the normal operation of the installations safety devices (valve, rupture disc) in 3% of the accidents in French refrigeration facilities (9% abroad) and 10% of the cases which are not refrigeration-related.

Operations involving the filling of installations and the transfer of ammonia between tanks also constitute dangerous phases. The risk is nevertheless greater in non refrigeration-related operations with 17% of the cases in France, for example (7% in refrigeration).

b) Failures reported

Failures	France (162)				Abroad (194)			
	R (91)		not R related (71)		R (44)		not R related (150)	
	Nb	%	Nb	%	Nb	%	Nb	%
Tank explosion not fire related in fire	- -	**-** **-**	1 2	**1.4** **2.8**	4 1	**9.1** **2.3**	19 6	**12.7** **4.0**
Pipe rupture (excluding hoses)	10	**11.0**	-	**-**	6	**13.6**	11	**7.3**
Hose / loading arm rupture	-	**-**	5	**7.0**	1	**2.3**	10	**6.7**
Small pipe rupture (purge, pressure gauge, etc)	3	**3.3**	-	**-**	-	**-**	-	**-**
Leak on tank or container	3	**3.3**	37	**52.1**	1	**2.3**	47	**31.3**
Leak on conduit or pipe	26	**28.6**	6	**8.5**	14	**31.8**	21	**14.0**

The accidents which occur on refrigeration installations originate from a pipe leak in 30% of the cases. This frequency is 3 times greater than for the other installations. However, these accidents are concerned more by leaks on tanks (52% of the cases in France, 31% abroad).

Only one explosion not caused by fire is documented in France. The accident occurred in Liévin in August 1988. During a fire, there were 2 tanks containing gaseous ammonia that exploded (domino effect). Several comparable cases are documented abroad.

The sudden rupture of pipes (excluding hoses and small-diameter pipes) with 11% to 14% of the cases ranks as the 2nd source of accidents. There appears to be less of this type of rupture for the other activities.

In non refrigeration-related operations, the rupture of a hose or a loading arm caused 7% of the accidents. This type of accident is directly associated with the frequency of ammonia loading or unloading operations. While presenting a low probability at the refrigeration installation level, this failure exists however during the first filling of the installations and, possibly, during significant topping up with ammonia.

c) Origin of the accidents

Origin	France (162)				Abroad (194)			
	R (91)		not R related (71)		R (44)		not R related (150)	
	Nb	%	Nb	%	Nb	%	Nb	%
Equipment failures of all types	**44**	**48.4**	**30**	**42.3**	**21**	**47.7**	**60**	**40.0**
Steel, fatigue or equipment defect	1	**1.1**	2	**2.8**	1	**2.3**	5	**3.3**
Corrosion	2	**2.2**	1	**1.4**	2	**4.6**	5	**3.3**
Vibrations / impacts / falling equipment	2	**2.2**	6	**8.5**	2	**4.6**	9	**6.0**
Leak / stuffing box, seal or flange rupture	7	**7.7**	15	**21.1**	3	**6.8**	9	**6.0**
Equipment failure (pump / compressor...)	5	**5.5**	2	**2.8**	4	**9.1**	7	**4.7**
Valve failure (rupture or leak)	5	**5.5**	2	**2.8**	3	**6.8**	8	**5.3**
Defective valves or discs	1	**1.1**	5	**7.0**	1	**2.3**	8	**5.3**
Clogging of a pipe	-	**-**	1	**1.4**	1	**2.3**	1	**0.7**
Product mixture or decomposition	-	**-**	4	**5.6**	-	**-**	5	**3.3**
Control / instrumentation / automatic control / electrical power supply fault	8	**8.8**	3	**4.2**	2	**4.6**	3	**2.0**
Ignition by spark / lighting / heating / motor / short-circuits	2	**2.2**	-	**-**	8	**18.2**	3	**2.0**
Loss of process control	7	**7.7**	8	**11.3**	3	**6.8**	7	**4.7**
Design or installation failure (welding...)	6	**6.6**	2	**2.8**	1	**2.3**	5	**3.3**
Insufficient maintenance (excluding corrosion)	6	**6.6**	2	**2.8**	-	**-**	-	**-**
Human factor (errors, instructions, etc.)	13	**14.3**	10	**14.1**	3	**6.8**	12	**8.0**
Vandalism, terrorism or deliberate acts	2	**2.2**	6	**8.5**	-	**-**	5	**3.3**
Sun, landslide, rain, tornado	1	**1.1**	1	**1.4**	-	**-**	3	**2.0**

Forty-eight percent of refrigeration-related accidents were initiated by at least one equipment failure. This frequency is comparable to that observed in non refrigeration-related activities (approx. 40%).

The information collected does not always allow the exact cause of the failure to be determined with precision:

- equipment failure or fatigue, corrosion, vibrations or impacts (6 to 13% of the cases),
- leaks on stuffing boxes, seals or flanges (piping, tanks) in 5% to 8% of the accidents on average. The high value (21%) reported for non refrigeration-related accidents in France is certainly attributable to leaks on transport tankers,
- failure of automatic control devices, instrumentation, etc. (2 to 8%),
- design error (2 to 7%),
- insufficient maintenance (2 to 6%),
- natural aggressions (1 to 2%).

All activities combined, failure concerns heavy equipment in 3 to 9% of the cases (pump, compressor, etc.), instrumentation and control (2 to 9%), a valve (3 to 7%) and a valve or a disc (1 to 7%).

The human factor can be blamed, at least partly, for 7 to 14% of the accidents due to:

- the lack of or poor operating or maintenance instructions,
- maintenance or servicing attempted with inappropriate tools,
- insufficient training,
- poor job site preparation,
- a misunderstanding of the installations or of the toxic risk that ammonia represents,
- the complexity of the installations and poorly identified equipment (configuration of valves, etc.).

The loss of control of the process during normal operation or during works is responsible for 5 to 11% of the accidents.

Deliberate acts or vandalism are responsible for 2 to 9% of the accidents.

d) Quantities of gaseous ammonia released

Refrigeration installations

The quantity of gaseous ammonia is known or can be estimated for 26 French accidents, while 66 cases out of 91 lead to a toxic release, and 12 foreign accidents (43 cases out of 44 accidents).

Quantities (t)	Q < 0.1	0.1 ≤ Q < 0.3	0.3 ≤ Q < 0.5	0.5 ≤ Q < 1	1 ≤ Q < 2	2 ≤ Q < 3	3 ≤ Q < 6
France	15	4	4	1	-	-	2
Abroad	3	1	2	1	3	1	1
Total and %	18 (47.4%)	5 (13.2%)	6 (15.8%)	2 (5.3%)	3 (7.9%)	1 (2.6%)	3 (7.9%)

Of these 38 accidents, 47% resulted in the release of less than of 100 kg of gaseous ammonia (small leaks on a seal, valve, etc.) and 76% resulted in a release of less than 500 kg (releases by valves, ruptures of small pipes of pressure tap or purge type, rupture of a pipe of 25 mm in diameter, a hole of 1 to 2 mm in diameter on the outlet of an evaporator, etc.).

Releases of 1 to 3 tons correspond especially to excess pressure and to a release by the pressure relief valves in large installations (fertilizer manufacturing plants, etc.), the rupture of a medium-size pipe or the unexpected opening of a shut-off valve. Above 3 tons, the release was caused by an equipment breakdown (exchanger, etc.), a break on a large pipe or a domino effect (installation engulfed in fire).

Miscellaneous activities (excluding refrigeration installations)

The quantity of gaseous ammonia is known or can be estimated for 40 French accidents, while 62 cases out of 71 can lead to a toxic release, and 57 foreign accidents (137 cases out of 150 accidents could have lead to a toxic release).

Quantities (t)	Q ≤ 0.1	0.1 ≤ Q < 0.3	0.3 ≤ Q < 0.5	0.5 ≤ Q < 1	1 ≤ Q < 2	2 ≤ Q < 3	3 ≤ Q < 6
France	16	6	2	1	2	4	4
Abroad	7	2	-	2	-	3	5
Total and %	23 (23.7%)	8 (8.2%)	2 (2.1%)	3 (3.1%)	2 (2.1%)	7 (7.2%)	9 (9.3%)

Quantities (t)	6 ≤ Q < 10	10 ≤ Q < 20	20 ≤ Q < 50	50 ≤ Q < 100	100 ≤ Q < 500	500≤Q<1000	Q > 1000
France	-	2	3	-	-	-	-
Abroad	1	6	7	13	8	2	1
Total and %	1 (1.0%)	8 (8.2%)	10 (10.3%)	13 (13.4%)	8 (8.2%)	2 (2.1%)	1 (1.0%)

The corresponding accidents are borderline with this study that concentrates on refrigeration installations. The were not the subject of in-depth study although a few general remarks can be made.

The dispersion of the quantities of gaseous ammonia released is linked to the wide variety of installations concerned.

The origins of gaseous ammonia leaks of less than 500 kg are comparable to those observed on refrigeration installations (small leaks on a seal or valve, releases by valves, ruptures of small pipes, etc.).

Releases of 1 to 3 tons also correspond to excess pressure and to a release by pressure relief valves in large-scale installations (fertilizer manufacturing, etc.) but also to hose ruptures or the failure of safety devices (discs, etc.) and to a long-term leak. The gaseous ammonia emissions between 5 and 15 tons were also initiated by hose ruptures or leaks on pipes following a failure or the unexpected opening of a safety device (disc, valve, etc.).

Releases between 20 and 100 t of gaseous ammonia are essentially linked to road or rail transport (collision, derailing of a tanker, including the more or less significant draining of a tank during unloading operations). Releases greater than 100 t were initiated by a rupture of a pipe (200 to 600 tons) or a large-capacity fixed tank.

Case study of typical refrigeration accidents

The cases presented below were retained to illustrate the typology of the main accidents likely to occur in a refrigeration installation.

1) Accident of December 2, 1994 (HOCHFELDEN - Bas Rhin)[36]

A gaseous ammonia leak occurred in the machine room of a brewery, during the replacement of a compressor intake supply line.

Description of the event: the manifold was isolated by closing 3 valves and purged at 7:25 am. At 9:15 am, during the operations, ammonia vapours were released from the manifold. The 3 technicians rapidly exited the machine room. The leak (consisting of 30 to 40 kg of gaseous ammonia) stopped 15 min. later, as soon as the fluids manager shut the intake system valves in a room adjacent to the machine room.

The fire brigade informed the residents living near the factory. No one was effected by the toxic release that was limited to the machine room. The room was able to be cleared of gas by forced ventilation (windows opened). The assemblers underwent hospital examinations but none showed signs of carry-over effects.

Causal analysis: the origin of the leak was rapidly identified. The leak originated from a shut-off valve that had been left open on the cooling system return line of the fermentation tanks. This error was not detected when the manifold was disconnected further to "EDF peak busy hour" load shedding (between 7 and 9 am) of 2 fermentation system pumps.

The ammonia spread into the machine room via the shut-off valve that had been left open during the automatic restart of the pumps at 9 am.

Lessons learned

- **Design of the installations - Ergonomics:** 2 points can be mentioned, one concerns the identification of certain equipment and the other, automated controllers.
  1. The shut-off valves are controlled by handwheels and are not identified (open / closed). The same is true for the piping and the fluid flow direction, which makes the structure of the installation hard to understand.
  2. The locking, lock-out of a device or a section of an installation requires a perfect understanding of the configuration and the operation of the various elements. The automatic and programmed

[36] Report by the Classified Installations Inspectorate.

starting of the pumps of an ancillary system shows the complexity of certain installations, the operation of which may not be fully understood. Can these pumps be stopped manually?

- **Operation - Maintenance:** the habit of working next to installations of this type and the commonality of the maintenance operations may lead to accidents of this type. The lack of simplified installation drawings and diagrams is certainly a handicap. These documents must be visible in the machine room and at the important locations within the installation.
- **Intervention:** the fitters were not seriously injured as they were wearing respiratory masks during their operations.

Reactions: the drawings of the refrigeration installation shall be updated and a thorough risk study, matched with preventive measures was undertaken.

2) Accident of November 21, 1994 (CONNERRE - Sarthe)[36]

An ammonia leak occurred near a community in a meat production facility being demolished.

Description of the event: the site had been abandoned for 2 years. The land had been purchased by the municipality in order to be rehabilitated. Following the work, 75% of the buildings were already flattened.

The accident occurred after an excavator ruptured a pipe. A security perimeter was set up. The accident was brought under control after 1 hour and 15 minutes. The unit seems to have been totally drained although no specific information was given as to the quantity of ammonia gas released. Eight people were effected, including 2 infants.

Causal analysis: the establishment was abandoned and no refrigeration company or other party claims responsibility for the installation. No drawing seems to exist. The job site was considered as a normal job site, and no special investigation appears to have been conducted prior to the start of operations.

Lessons learned

- **Organisation:** the operations were not sufficiently prepared. The installation was not secured (was even its existence known?).
- **Intervention:** The workers in charge of the demolition operations had neither protective clothing nor gas mask. The rescue operations were long and the unit had to be totally drained before it could be controlled.

Reactions: the job site was postponed until an expert evaluation of the installation could be conducted.

3) Accident of August 11, 1994 (REIMS - Marne)[36]

An industrial establishment wanted to definitively shut down a refrigeration installation, which had been inoperative since 1990 and contained about 280 kg of ammonia. The operations were conducted by 2 external companies.

Description of the event: Initially, two technicians recovered 250 kg of liquid ammonia in 8 steel cylinders that were specially prepared for the operation. The drainage of the gaseous phase was then conducted by immersing pipes, connected to the installation's branch connections, in a plastic bucket filled with water. When saturated, the ammoniated solution obtained was poured without prior dilution (certainly several times), into the nearest rainwater gutter opening.

The fire brigade was informed by a resident who detected the smell of ammonia coming from the city's sewer system. They immediately informed the Water Utility in order to alert any personnel possibly working in the sector.

Causal analysis: the sewer pollution resulted from a deliberate act. The liquid ammonia drainage operation was well prepared (specific receiving cylinders, etc.) and was performed correctly although the degassing of the installation was not performed according to the same strict guidelines. The ammoniated solution poured into the sewer degassed slowly and the gaseous ammonia exited the drainage outlets all along the pipe.

Lessons learned: the accident appears to be relatively minor but provides a certain lessons.

- **Organisation:** the establishment did not control the work being conducted by the external companies; it appears that the job site was not monitored by a refrigeration specialist from the plant.
- **Training:** the indirect risks were under estimated during the installation degassing operations (possible intoxication of sewermen, the risk of a confined explosive atmosphere, toxic release into the environment upon leaving the pipe).
- **Intervention:** a single cartridge type gas mask (inappropriate for a massive toxic gas leak as it would be saturated too quickly) was available for two technicians. The workers had no specific protective clothing whatsoever.

Reactions: the firemen installed a voluminous tank to ensure greater dilution of the ammoniated solution before releasing it into the wastewater system. It would be desirable that a more "technical" recovery (neutralisation prior to release, etc.) of the gaseous phase be implemented by this type of "specialised" contractor.

4) Accident of June 13, 1994 (NANTERRE - Hauts de Sienne)[36]

In an old ice cream factory where only the head office is maintained (no industrial activity is performed at the site), a gaseous ammonia leak occurred during the dismantling operations on an old refrigeration installation.

Description of the event: the refrigeration installation, declassified in 1978, had been shut down for roughly fifteen years. During overhaul operations of the building's ground floor, the architect in charge of the modifications "discovered" it hidden in the records room. The installation was distributed over 2 levels: 2 evaporators and a liquid cylinder (approx. 4 m^3) in the zone of operations, 3 compressors, 1 condenser and a receiver in a small adjacent room.

On May 25th, the architect informed the Prefecture. The 4 m^3 tank appeared to contain ammonia(pressure of 6 bar read using a pressure gauge), all the other pressure gauges indicate that there is "no pressure" in the circuits. The administration requested that the installation be neutralised by a specialised firm. On June 13th, the architect indicated that the installation's neutralisation operations were conducted on Saturday, June 11th. The product recovered by bubbling with water was to be disposed of in an authorised waste centre.

The ammonia leak occurred June 13th at 3 pm when a foreman attempted to dismantle a partition separating the 4 m^3 tank from an evaporator. His pick axe cracked a pipe (∅ 40 mm) connected to the tank's low point.

A safety perimeter of a few hundred meters was set up: The emergency response personnel could not intervene without protective clothing or gas mask. Roughly sixty people in the establishment were implicated, 16 were hospitalised including 3 that had to be hospitalised overnight. The company that performed the neutralisation operation was called back.

The gas leak continued until the installation was completely drained and ended at 9 pm. According to the administrative archives, the ammonia tank had a capacity of 400 kg; the quantity of ammonia release is not known.

Causal analysis: the establishment had "forgotten" about the existence of a dangerous installation on its site. The installation was not secured when abandoned (drainage, degassing, etc.).

Prior neutralisation of the installation was conducted without checking all of the circuits and equipment.

The leak that occurred when the pipe was pierced was probably supplied by the drain line from a condenser connected to the tank.

Lessons learned

- **Environment of the installation:** the installation was no longer used. The facility was converted without any precaution relative to the archival storage room. The risks were aggravated (no inspection, no maintenance, potential fire, etc.).

- **Organisation:** a drawing of the unit was not available on site and no managerial staff seems to have a "technical" memory of the installation. The renovation of the facility seems to have been entirely "delegated" to an external party (the architect). The installation's securing operations were carried out on a Saturday. It was an end of week period for the contractors but the number of employees in the establishment was less.
- **Intervention:** neutralisation was conducted by an external company not familiar with the installation. The operations were conducted without the refrigeration expert of the proprietary company being present and without a detailed drawing of the unit.

When the pipe was ruptured, the job site superintendent was persuaded that the installation had been degassed and no safety measures were taken.

The ammonia leak was not stopped, and lasted 6 hours until the installation was completely drained.

Reactions: the installation was dismantled.

5) Accident of March 11, 1994 (SAINT BRANDAN - Côtes d'Amor)[37]

A significant leak of gaseous ammonia occurred in a poultry slaughterhouse when an employee was supplying a freezing tunnel.

Description of the event: the operator was using an electric pallet truck and collided with a refrigeration circuit purge line. The pipe broke. The alarm was not raised immediately and 500 kg of liquid ammonia - 40°C spilled onto the floor. The tunnel door was open. The spilled liquid began to evaporate and progressively entered the facilities which were evacuated as soon as the first odours were detected. Three employees were intoxicated. One individual, who was more seriously effected, was hospitalised.

Causal analysis: a fault tree established by the INERIS is enclosed in Appendix 8. The purge's protection had already been subjected to impacts previously and was weakened. The downgraded situation was not identified. Two hypotheses are plausible.

1. The operator did not pay attention to the fact that he ran into the pipe. He had already run into it several times and was not aware of the risk. The pipe had already become weakened after numerous impacts and no corrective action had been taken.

---

[37] Study of accidents involving ammonia and conducted jointly with the INERIS (Mmes ABIVEN & BAUCHET - December 1994) and reports from the Registered Installations Inspectorate.

2. The width of the isles reserved for handling, near the refrigeration installation and the choice of the protective barriers are at issue in this accident.

Lessons learned

- **Design of the installations - Sizing - Ergonomics:** sensitive installation equipment (purge line) without time-tested efficient and reliable protection.

  A "sensitive" part of the installation was not or was insufficiently identified. The possible risk was not identified.

  Access to the freezing tunnel was poorly dimensioned or the transport equipment was inappropriate (size, manoeuvrability, etc.).

- **Operation - Maintenance:** monitoring of the installation's condition and especially the safety devices protecting sensitive equipment was insufficient.
- **Training:** the employees were not sufficiently trained in terms of the risks involved with the installation and the measures to take if an ammonia leak should occur (inform the supervisory staff, etc.).

Reactions: the physical protection of the purge was reinforced (low "bumpers" with railing a sufficient distance from the evaporator pipes). The personnel's awareness must be raised relative to the risks that ammonia presents and the immediate actions to be taken in case of a product leak (alarm, etc.).

6) Accident of February 17, 1994 (DUCEY- Manche) [37/38]

A violent fire destroyed a cheese factory considered to be the most modern in Europe.

Description of the event: the factory was operating in three 8-hour shifts, monitored by roughly twenty employees (170 during the day). A maintenance worker discovered the first flame at 4.15 am behind a packing machine. Three employees came with fire extinguishers but rapidly had to abandon their efforts. The fire grew, releasing thick irritating smoke. The plant was evacuated and the Ducey volunteer fire department was called at 4.22 am.

All available vehicles were called in compliance with the intervention plan. The site foreman had worked for many years in the factory (maintenance of the installations) and had in-depth knowledge of the sensitive points. The buildings have a total surface area of 15,000 m². The buildings are imbricated and cut up into cells, much like a labyrinth. The walls and ceilings are filled with polyurethane foam in order to maintain the temperature and the humidity level in the air. Ten tons of ammonia were present in the refrigeration installations, 20,000 l of soda and 130,000 l of heavy and light fuel were also stored in the establishment.

---

[38] Magazine FACE AU RISQUE No. 303 (R. DOSNE - May 1994).

The firemen began fighting the fire at 4.34 am. As reinforcements arrived, the firemen attempted to stop the flame front that was progressively entering the core of the factory without encountering an obstacle. The flames spread through the walls and ceilings, fed by the dense and insulating foam ensuring their stability. Additional reinforcements were requested at 5 am considering the violence and rapid progression of the flames, as well as the toxic gases released. The central building's metal structure collapsed progressively. It was impossible to penetrate the facility. The visibility was zero due to the smoke and the unprotected metal structure began to become weak. The nozzlemen attempted to progress despite the smoke, heat and collapsing structures; everyone was wearing self-contained breathing apparatus. Progressively, 80 men were deployed around the site without being able to contain the fire which rushed through 12,000 of the plant's 15,000 m² of surface area in 3/4 hour.

At 7.22 am, 7 response centres were engaged. The fire-fighting means were concentrated toward the only masonry wall, at the back of the building, and which separated the workshops from the administrative part of the plant. It was not a firewall, although its presence represents an obstacle. Doors were opened in this wall in order to install 6 nozzles and set up a water curtain. This strategy was able to save the factory's administrative and computer facilities and the pre-treatment workshop and its 20,000 l of soda. On another side of the building, the packaging storage facilities housing the power plant were also saved.

The fire was brought under control at 10 am. One effected fireman was hospitalised, 15 slightly effected employees and a fireman with superficial burns on a hand were cared for at the site. The fire continued to consume the coolers in which 2.5 million cheeses were kept. The lack of access and vents still hampered the intervention. The rubble was sprayed down throughout the day while sporadic flames burned the twisted sandwich panels where a bit of foam still remained. The operations were completed at 8 pm.

Causal analysis: the exact cause of the fire is not known although its rapid development can be attributed to the insulating materials in the coolers.

"For hygiene and insulation reasons, the food industry proposes rot-proof, acid-resistant walls which endure frequent washing. The sandwich panel consisting of 15 cm of rigid polyurethane foam between 2 aluminium or polyester sheets is one of the materials that meet these criteria. The material offers excellent heat insulation, good mechanical qualities (stiffness) and a low weight/m² ratio (lightened structure) at a reasonable cost).[38]

Lessons learned

- **Design of the installations:** the widespread development of the fire is due to lack of masonry walls (the fire was stopped everywhere where there was one). The sandwich panels have adverse effects. The foam used in their construction feeds the fire which then travels between the walls and can't be reached by the nozzles.

  In addition, the installations can be very compact and criss-crossed by numerous pipes, some of which conveying toxic products (the refrigerant, in particular), thus complicating the access, traffic areas and the implementation of rescue means. The vastness of the installations lead to significant lengths of refrigerant transport piping, without a sufficient number or few shut-off devices, can also reduce the efficiency of rescue operations (accident of June 17, 1992 at SECLIN above).

- **Knowledge of the installations - Intervention:** all intervention operations in such an environment are difficult despite the rapidity of the alert.

  The employees reacted quickly although were unable to control the outbreak of fire.

  The senior director of emergency operations knows the factory perfectly. The initial rescue means can be placed as well as possible in order to save what can be saved and to avoid aggravating the accident and a domino effect (explosion of tanks containing ammonia, fuel tanks, etc.).

  In case of fire, the rendezvous was located downwind, in the axis of irritating smoke. Four employees who went missing during the initial minutes of the intervention had preferred to regroup elsewhere.

Reactions: the activity restarted at the damaged site. The factory was rebuilt by separating or dividing up the various units.

Generally speaking, the insulation foams, essential in refrigeration storage facilities, present problems due to their flammability. These problems can be solved by adapted construction practices (fire walls, physical protection of insulation by angle sections, door frames and sealants, etc.).

In addition, installation inspections and fire drills must be organised regularly between the establishments concerned and the public emergency response teams. Regularly updated drawings must also be provided (within the scope of an internal contingency plan, etc.).

Considering the rapid spread and potential size of the fire, a sufficient quantity of water must be available nearby to enable extensive fire-fighting means to be engaged rapidly. A catchpit must be able to collect the fire-fighting water that may be polluted. This water may possibly be recycled during the fire, forming an additional source of water.

7) Accident of May 17, 1993 (GUERLESQUIN - Finistère)[36]

A stream was indirectly polluted following an ammonia leak in a poultry meat production plant.

Description of the event: a release of ammonia occurred at 9.30 pm lasting 20 min., from a valve located on the roof of a building housing the compressors of a refrigeration installation. The quantity of ammonia released is not known.

Part of the ammonia evaporated into the atmosphere, while the rest likely drenched part of the roof. A violent thunderstorm washed off the roof and directed the residual ammonia into the rainwater sewer. This sewer leads to a stream at the level of the physical-chemical pretreatment station above the community treatment plant. The accident does not appear to have significant consequences on the environment.

Causal analysis: the ammonia leak initiated from a fault on a solenoid valve and overpressure in the refrigeration installation.

Lessons learned

- **Environment of the installation:** a refrigeration installation can indirectly be the origin of ground water pollution. The ammonia leak came from a valve but all other unchanneled release (purge, leak on a pipe, etc.) could have had the same consequences.
- **Design of the installations:** the safety valve with release at roof level, designed for the safety of individuals, is compliant with regulations governing pressurised gas equipment. The valve is designed to collect toxic releases and directs them to a point where they are no longer dangerous, especially for the personnel, but require no specific treatment of the release.

Reactions: the operator changed the faulty solenoid valve and the safety valve. A study was conducted designed to connect all of the safety valves located on the roof to a cylinder and trap all occasional purges.

The occasional releases from the safety valves could be neutralised (spray boom, washing, etc.) or incinerated (flare-stack).

Continuous monitoring of the effluents from the rainwater and wastewater sewers may be planned (pH or ammonium detection).

8) Accident of June 17, 1992 (SECLIN - Nord)[36/37]

In a dairy, a fire ripped through 2,000 m² of a building used to store paper, cardboard and plastic packaging.

Description of the event: the fire started around 1.15 am. It was discovered during a security round and the alarm was given within the following 10 minutes. The fire spread to 2,000 m² of a building in which 1,500 m^3 of packaging was stored (the authorised volume was 210 m^3).

An ammonia pipe passes through the building, which was formerly used as a cooler. Since the new use of the building and in order to take the expansion batteries out of service, these pipes were plugged 2 m from the gable inside the building, but were never drained. The fire reached the ends of the pipes in a cul-de-sac.

In order to prevent the risks caused by excess heat and deformation, these ends had to be isolated from the rest of the refrigeration installation that contained 7 t of ammonia. Operations were undertaken at the exit of the cooler, in a zone protected against fire and located above the awning covering the passageway between the cooler and the warehouse. An initial plugging operation using caps was started in the morning on the "expansion" pipe (2.2 bar in gaseous phase, ∅ 60 mm). The caps were welded after degassing of the section of pipe concerned (approx. 60 m), isolated after the shut-off solenoid valves had been closed (around 2.30 am) resulting from the electrical power supply failure. The firemen were informed of the intervention. Early in the afternoon, after closing the manually-controlled shut-off valves located in the pipe gallery, a 2nd plugging operation was started by cutting the supply line (3.5 bar in liquid phase, ∅ 33 mm). An abnormal quantity of ammonia appeared at that time. The operator moved away to close the upline valve on the circuit near the compressor located in a building 100 m from there.

During his absence, the firemen who were monitoring the rubble had a shift change at noon. The lieutenant of the arriving crew was intrigued by the white clouds that were developing above the awning. He approach to within approximately 10 m and came into contact with a cloud of ammonia. He was evacuated to the clinic. Thirty minutes later and after complete degassing, a sleeve was welded. This operation proved difficult due to the presence of residual ammonia. During the supply line degassing operation, approximately 60 l of ammonia vaporised.

The cost of damages was evaluated at 20 MF.

Causal analysis: a fault tree established by the INERIS is enclosed in Appendix 8. The origin of the fire was not explained. However, traces of a break-in were noted on the fencing of the property.

The fire developed in a warehouse next to the refrigeration installation. Firefighting operations had to begin by closing certain pipes that had remained unpurged and out of use for a long time. There were 2 pipes between the warehouse (the former cooler) and the refrigeration installation in operation. One of them was purged and isolated without difficulty. The 2nd pipe was purged and major operations were necessary to isolate it.

The ammonia leak was linked to insufficient sealing of the shut-off valves. Alone when the line was being isolated, the operator had to leave the work area to close a general supply valve located 100 m away. Insufficient organisation of the rescue effort lead to the intoxication of one of the rescue personnel. The fireman on duty was not informed of the operations being performed by the company and by his co-workers during the shift change.

Lessons learned

- **Environment of the installation:** the cooler was being used as a general storehouse without first being sufficiently secured (the unused pipes were neither dismantled nor purged).
- **Design of the installations:** the widely spaced layout of the installations can lead to significant lengths of refrigerant transport pipes. They are thus difficult to shut if the shut-off means are faulty, insufficient in number or not adequately automated.
- **Operation - Maintenance:** in-service checks must be frequent and regular. They must allow operation of sensitive equipment to be checked (shut-off valves, safety devices, etc.), particularly on little-used or unused sections of the installations.
- **Knowledge of the installations - Training:** the operator is familiar with the refrigeration installation as he knows how to isolate it. Just one person, however, seemed to have in-depth knowledge of the installations, the drawings of which were not up to date.
- **Intervention:** the intervention encountered numerous difficulties. These difficulties were not due to the violence of the fire itself, but to the operations conducted to secure part of the installations. Pipes must be drained and degassed and the valves are not hermetic. Major operations are required.

  Poorly degassed pipes can lead to a risk of ammonia explosion, especially if welding operations are required to isolate the insulation.

  The entire accident zone and the entire circuit should have been locked out considering the nature and the amount of work to be done on the refrigeration circuit. An error was committed when the technicians relied on a single valve to shut off the circuit. The valve was not hermetic and a firemen was intoxicated.

Reactions: it was requested that a study be conducted to evaluate the risks associated with the connectedness of the refrigeration installations and the boilers located in the same building, as well as the distribution of ammonia both inside and outside the buildings housing refrigeration equipment. This study must enable which additional measures must be taken (additional shut-off valves, ammonia detectors, automatic valve closing devices, etc.).

The refrigeration equipment was accessed by an independent organisation. A thorough periodic inspection of this equipment was requested, and the time between 2 inspections must not exceed 6 months. Technical personnel, specifically trained in the make-up and operation of refrigeration installations, must be able to be contacted at all times.

Liquid phase piping on an installation pending authorisation is to limited to 50 mm in diameter.

9) Accident of July 18, 1991 (LANDERNEAU - Finistère) [39]

An ammonia leak occurred in the machine room of a refrigerated storage facility.

Description of the event: the accident occurred 40 min. after the installation was started. The employees of a neighbouring plant were effected and raised the alarm to evacuate their establishment; 5 of them were hospitalised.

Equipped with a protective mask, an employee of the warehouse actuated the installation's emergency stop and noted that the leak was coming from 2 safety valves:

- the HP manifold valve on the condenser inlet,
- the oil refrigerant valve of a compressor on the HP pipe branched at the exit of the HP fluid tank.

Causal analysis: the ammonia release occurred following the failure of the injection solenoid valve of a MP cylinder. Placed back into service, this solenoid valve operated normal a few times in manual then in automatic position. The valve's failure, over an undetermined period of time, resulted in choking of the HP circuit (tank and condenser) and the opening of the safety valves. The wind blew the ammonia cloud toward the neighbouring plant.

Lessons learned

- **Environment of the installation:** another plant is located near the establishment. No mutual information exists concerning the risks presented by the installations.
- **Design of the installations:** the detection and alarm devices were insufficient. The operator was indirectly informed of the accident by the employees of a neighbouring plant. The accidental releases by the valves can be significant and are not treated.

---

[39] Operator's accident report.

- **Servicing - maintenance:** the periodic checks conducted on the installation were not enough to prevent a "transient fault" from appearing. The fail-safe configuration of major safety-related equipment is a necessity.
- **Intervention:** internal ammonia / fire drills are organised regularly. The operator reacted correctly to the situation.

Reactions: the solenoid valve was replaced as a precautionary measure, as was the HP safety pressure switch on the compressor and the valves which operated (their efficiency was questioned).

The HP safety pressure switches were doubled by a general HP safety pressure switch on the general HP manifold. This pressure switch is set at an intermediate cut-out pressure between the pressure switches of the HP compressors and the operating pressure of the HP circuit's safety valves.

Exercises are organised with the neighbouring plant.

10) Accident of October 11,1990 (MONTELIMAR - Drome) [37/39]

A refrigeration installation shut down during the night in a refrigerated warehouse. An ammonia leak occurred when it was restarted in the morning.

Description of the event: when work started again, the supervisor noticed that the refrigeration installation was stopped. He checked the various equipment, noted a high liquid level in the MP tank but he felt that it wasn't dangerous and started the HP compressor normally. When the control system triggered the LP compressors, the HP compressor drew in liquid ammonia and burst. A large quantity of gaseous ammonia was released.

The supervisor present turned off the electrical power supply but had to wait until the firemen arrived to go with them into the machine room and close the shut-off valves on the faulty compressor. All of the required equipment, namely protective garments, masks and air cylinders were available on site.

The firemen recorded 15 to 25 ppm of ammonia in the neighbourhood located to the south of the warehouse. They evacuated homes, a supermarket and the city's technical services. The situation returned to normal in the neighbourhood 2 hours later.

Causal analysis: a fault tree established by the INERIS is enclosed in Appendix 8. The installation was shut down following a control problem.

The compressor had not been checked since May 1987. A burst disk in the compressor had allowed communication between the intake and discharge. The disk in the discharge manifold was found to be destroyed (following the depressurisation induced by the rupture of the casing?). The coil of the motorised valve separating the MP tank and the LP tank was faulty. The operator could not indicate if the valve had remained open or closed.

The rupture of the compressor casing could be attributed to the combination of several factors (failure of a motorised valve, excess pressure to the compression of liquid ammonia, thermal shock during the start-up phase, etc.).

Lessons learned

- **Environment of the installation:** owing to the activity, this type of establishment is often located within or in the immediate vicinity of the urban fabric. Public information and the creation of an internal contingency plan and special intervention plan are to be considered depending on the size of the installation and the inherent risks (fire / toxic release).
- **Design of the installations:** the refrigeration installation did not have sufficient safety features (lack of a high level alarm on the tanks, no check valve, pressure switch on the compressor, automatic shut-down of the installation in case of excess pressure).
- **Operation:** there was no installation restart procedure after triggering.
- **Maintenance - Servicing:** what state was the compressor in at the time of the accident? An accident already occurred on the installation in August 1990 following a shut-off valve failure (accident of August 1, 1990 below). The time between 2 compressor inspections (or possibly other equipment) must not be too long.
- **Intervention:** personal protection must be sufficient, which is not the case when only cartridge-type masks are available.

Reactions: the operator must define an inspection schedule for the equipment. Inspection frequency must not exceed 1 year.

Burst disks, the rupture pressure of which is connected with the installation's true operating pressure, a check valve between MP and LP tanks and a level sensor in the MP tank (to prevent the compressors from starting if the liquid level exceeds a given threshold) shall be installed.

11) Accident of October 8, 1990 (DIEUE-SUR-MEUSE - Meuse) [37/39]

An ammonia leak occurred on a refrigeration installation in an ice cream factory.

Description of the event: at around 6.30 pm, a leak of 50 l of oil then 350 kg of ammonium occurred on one of the 4 compressors located in the basement of the refrigeration installation. The installation contained a total of 1,000 kg of ammonia. The leak occurred at a pressure of 10 bar, then at 2 b via an opening with a diameter of 22 mm.

Factory personnel, equipped with cartridge-type masks, intervened immediately to close 2 valves located on the inlet and discharge sides of the compressor. The extent of the leak did not allow them to close 3 "Tee" valves located on the hot gas return circuit (dry ammonia vapour at 60°C) on the upper part of an oil separator.

The firemen arrived at 8.00 pm and managed to close the 3 valves. For safety reasons, company personnel was evacuated although the following crew was able to go to work at 9.00 pm. The installation was checked and put back into operation the following day.

Causal analysis: a fault tree established by the INERIS is enclosed in Appendix 8. The rupture of a sight glass used to check the condition of the oil circulating in the compressor is at the origin of the ammonia leak. This indicator is located upline from the compressor and had been replaced during its last overhaul.

The valves of the compressor can be closed while the others remain open. The hot ammonia of the "freezer" installation was discharged by the open valves and entered the oil separator. The separator was empty, the ammonia exited by a pipe at the low point and exited via the broken sight glass.

Lessons learned

- **Design of the installations:** the "freezer" outgoing lines were not equipped with a check valve. To isolate the installation, numerous valves must be closed and they cannot be shut-off remotely. The complexity of the circuits, the high number of shut-off devices to be operated and a lack of automated controllers complicated the intervention.

  The MALMÖ-SKANE accident (SWEDEN) which occurred on a refrigeration unit in a chemical plant on October 29, 1989 (case No. 133), is also particularly illustrative. A 300 mm crack on a pipe lead to a 5 t leak of ammonia and the formation of a thick aerosol in the building. Stopping the leak required 20 valves to be closed and the intervention of 15 people. The rescue services had to first prepare for the operations and the manoeuvres required in a comparable installation nearby. Three attempts were required to stop the leak.

- **Maintenance - Servicing:** the control tube burst although it had been replaced during overhaul operations. Was a check of the spare parts conducted (faulty tube)? Was poor installation noted (instructions, tools used, etc.)?

- **Knowledge of the installations - Training:** the compressor intake and discharge valves can be closed by creating a vacuum in the installation. There is no automatic lock-out system. Do intervention instructions exist?

  The personnel lack emergency intervention training and knowledge of the installations.

- **Intervention:** the available equipment does not allow long-term intervention. This equipment must be adapted to the risk (cartridge-type masks are not sufficient as they can be come rapidly saturated during a major ammonia leak). Hermetic equipment (totally encapsulated suits, PBA) must be made available to the operators who are trained to use them.

Reactions: the implementation of stronger ventilation with processing of the residual effluent can be considered, as well as valves with check valves and remote shut-off means.

12) Accident of October 3, 1990 (MONDEVILLE - Calvados)[40]

A fire was reported in a refrigerated warehouse that was undergoing retrofitting operations.

Description of the event: the accident took place during operations essentially involving the retrofitting of the lighting's electrical installation and to improve the thermal insulation of the coolers. The 3 coolers involved did not contain merchandise.

The fire was reported at 12.10 pm when all the workers had left for lunch. The alarm was raised 15 min. later by the warehouse supervisor who lived across from the warehouse. The firemen arrived rapidly at the site and brought the fire under control at 2.30 pm. There was not an ammonia leak resulting from the fire.

Causal analysis: The fire started in a cooler where the old lighting had been removed and the new lighting was partially put back into service. The thermal insulation was improved by spraying polyurethane foam onto the cooler ceilings. The operation was illuminated by a powerful halogen spotlight which was normally unplugged after each work session. This spot light may be cause of the fire.

---

[40] Note of the Registered Installations Inspectorate established according to an assurance adjuster's report.

Lessons learned

- **Design of the installations:** the flammability of the materials making up the insulation, particularly when the latter are not protected (coolers being overhauled) is again noted.

  The fire was stopped by a wall of cement blocks separating the coolers from the machine room (see accident of February 17, 1994 - DUCEY).

- **Job site monitoring and instructions:** the risk of the insulating foam catching fire during work is underestimated. Were specific instructions provided? Is the job site sufficiently monitored?

13) Accident of August 1,1990 (MONTELIMAR - Drome)[37/39]

An ammonia leak occurred in a refrigerated warehouse during a maintenance operation on a refrigeration installation.

Description of the event: a faulty valve had to be replaced on the LP circuit of a refrigeration installation. After having inspected the installation at the site, the technician neutralised the section of the circuit where the faulty valve was located.

Wearing a mask, the technician loosened the valve to finish purging the gaseous ammonia circuit. This operation generally lasts twenty or so seconds. The operator noted that the flow from the purge was progressively increasing instead of decreasing and decided to rapidly close the valve. He took the ratchet wrench that he left under the valve but was unable to use it as it became seized when it came into contact with the jet of cold ammonia. As his mask started to become saturated, he decided to put on a protective suit and a mask equipped with compressed air cylinders (4 masks and 2 complete systems are distributed around the warehouse). Only once he was properly equipped and had a new wrench was he able to tighten the valve and stop the leak. The machine room's rear door was left open throughout the incident.

According to the operator, the leak was not major; it lasted roughly twenty minutes and released 3 to 5 l of ammonia (1,200 l in the installation). The toxic gas exited the room via the open door and spread along the building, in the direction of the first homes located to the south. A pregnant woman was unwell and had to be hospitalised.

Causal analysis: a fault tree established by the INERIS is enclosed in Appendix 8. The refrigerated warehouse manager was on holiday and the work was delegated to the maintenance department manager. As the technician did not find the drawings of the system and did not know about the pipe connecting the medium pressure network to the low pressure network on which he had to work. A solenoid valve opened on the neutralised pipe, and allowed liquid ammonia to exit.

Protective equipment and inadequate tools increase the duration of the ammonia leak. The machine room had 2 exits. One leads into the warehouse area and the other leads to the dock at the rear of the building. This 2nd door is always left open to ventilate the machine room. The existing mechanical ventilation is insufficient (1 small fan).

Lessons learned

- **Design of the installations:** the ventilation of the room was insufficient and a door was left permanently open to aerate the building. The passive protection that it represents (confinement) was inoperative.
- **Maintenance - Servicing:** the LP circuit valve was leaking. Were preventive checks performed on the installation? What was the inspection interval?
- **Organisation:** the operator was alone at the time of the intervention. No instructions were given for holiday periods. There was no "on-call" organisation in case the shop supervisor was absent. Knowledge of the installation relied on a single person and no longer existed when that person was absent.
- **Knowledge of the installations - Training:** the operator was not familiar with the installation and did not identify the HP / LP line. Installation diagrams were not available. Knowledge of the risks associated with this type of installation were insufficient. The consequences of the actions performed on the installation were not identified.
- **Intervention:** the tooling (ratchet wrench) was not adapted to the operation being performed (rapid seizing due to the cold).

The personal protection means (cartridge-type gas masks) which rapidly become saturated are not adapted. Adapted means (PBA, hermetic suits) were present on the site but the operator had encountered difficulties getting equipped by himself.

Reactions: the main modifications concerns the installation of the compressors and the electrical installations (transformers, etc.) in separate rooms, the installation of an efficient ventilation system with a double activation threshold with an exhaust stack on the roof, enlargement of the catchpit underneath the compressors and modification of the machine room exits.

SUMMARY OF THE INFORMATION GATHERED - BIBLIOGRAPHIC STUDY

Risks

Ammonia refrigeration systems and the related installations (warehouses, coolers, etc.) present 2 main risks:

- a toxic risk associated with the more or less significant quantity of ammonia used as a refrigerant. More than 73% of the French accidents studied (98% of the accidents abroad) lead to the release of ammonia.

  In 52% of the French accidents studied (93% abroad), the toxic gas was released into the atmosphere. It could also lead to water pollution after being spilled in to the sewer system (pure ammonia or in solution with water resulting from installations rinsing, cloud neutralising or fire fighting efforts). In France, this type of pollution is recorded in 18% of the cases.

- a fire risk (34% of the accidents recorded) linked essentially to the use of a large quantity of more or less combustible insulation materials.

  The first insulation material used cork; fires were thus difficult to extinguish and could smoulder for days. The risk, however, was low in relation to that resulting from the adoption of polystyrene or polyurethane foam insulation, especially if they are not "self-extinguishing". A fire can spread rapidly while releasing very toxic fumes [41].

  Finally, the merchandise itself (frozen meat can burn intensely if it is exposed to a major source of heat long enough, for example) and packaging could keep the fire burning.

a) Toxic risk [42/43]

[41] Fire prevention and safety in cold stores
(A.E.E.F. / I.I.R. Commisssion D11 - 1982).

[42] Ammonia used as coolant (INTERNATIONAL INSTITUTE OF REFRIGERATION I.I.R. / I.I.R - 1993).

During normal operation (excluding defrosting), the mass distribution of the ammonia in a refrigeration installation is 10% in the HP tank (50% during evaporator defrosting operations, 1 to 2 times/day, i.e. 8 hours/day), 20% in the LP tank, 20% in the pipes and 50% in the evaporators[44].

- With nearly 30% of cases known, pipe leaks represent the main source of incidents and accidents.
- The instantaneous rupture of a pipe is not a rare event. This type of accident represents 11% of the accidents in France (14% abroad). The largest liquid phase pipe is generally the one that connects the installation's low pressure pumps to the evaporators. The flow of ammonia is high (n times the vaporised output) although the pressure is relatively low (3 to 4 bar above the evaporation pressure). Except for a few segments, this pipe which is generally located inside buildings, can be less dangerous than a condenser / HP liquid tank connection located outside of all confined rooms.

  A pipe can sometimes break due to excess pressure generated following incorrect operation, a design error or incorrect pipe configuration. Excess pressure increases the risk of shock wave propagation into the liquid pipes. The shocks essentially occur when the defrosting cycle using hot gas from low temperature systems and most often, either during the opening, at the end of the defrosting cycle, of the intake shut-off valve (shock wave in the liquid intake line), or upon opening, at the start of the cycle, of the hot gas solenoid valve (shock wave in the coil).

  Serious accidents can also be caused by water hammering of gouged or cracked pipes; thus requiring a good quality weld throughout the entire thickness of the pipe[42].
- Following an incident or maladjustment of the LP part of the circuit, "liquid hammering" could also occur if the oil, liquid ammonia or a mixture of the two suddenly flowed into the compressor cylinders. The liquid's incompressibility could cause the compressor head to rupture. In order to prevent this serious hazard, the Ministerial Decree of 04/25/79 requires the installation of an anti-hammering device to ensure automatic decompression in each cylinder before the internal pressure reaches an excessive level. The decompressed fluid can be returned into a section of the installation at lower pressure or to a safety device (valve, safety tank upline from the compressor, etc.). This decompression device is not mandatory for hermetic and helical rotary compressors, as well as for compressors whose sweep rate per cylinder is less than 25 m^3/h. A valve placed between high and low pressure must also protect the compressor in case the discharge valve is accidentally closed during normal installation operation.

---

[43] Guide d'étude des risques technologiques, Technological risks study guide (AFF / Club Ammoniac - 1995).

[44] Réunion S.E.I. / Profession of July 27, 1993 (meetings of August 4, 1993).

- Ammonia is a powerful solvent which, when being loaded, captures dust, scale, sand and residual humidity, in the pipes, tanks, valves and other components [53]. Regular and careful cleaning of the installation must be performed during assembly operations (rotary metal brush, compressed air or nitrogen, etc.).

- In refrigeration, the instantaneous loss of containment on an ammonia tank is reported in 9% of the foreign accidents although no example is known in France. The HP accumulator cylinder, generally located outside buildings, represents the most sensitive point of the installations. It contains ammonia at the highest pressure and its volume can have an overriding effect in the determination of joint action distances (urbanisation, special intervention plan). Other tanks (MP or LP cylinders, evaporator shells, etc.) have lower service pressured despite often much larger volumes and are generally confined inside buildings.

- Stress corrosion cracking has sometimes been observed in the ferritic steal used to manufacture ammonia tanks. Such cracks, often at the origin of ammonia leaks, were noted in refrigeration installations. The presence of a few ppm of oxygen in the liquid ammonia or a few thousandths of ppm in gaseous ammonia is sometimes enough to cause these cracks. As a result, air must be entirely purged from the installations.

  A minimal water content of 0.2% in ammonia helps prevent these cracks [45]. The HP side of a compression system is the most sensitive as it often has a water content less than 0.2%. Finally, the risk of cracks is lower at temperatures below - 5°C and in tanks made of carbon steel with low drawing resistances (less than 350 N/mm²) which were annealed after welding.

- Contrary to the old practice, the high pressure safety valves must not be connected together by a common manifold, the exterior end of which is directed downward to prevent rainwater from entering. The gas should preferably be released upward at high speed in order to promote dispersion [52].

- A Swedish study[46] indicates that the major part of the leaks are located on the LP side where there is often a vacuum. The origin of these leaks is often one of the following:

  - an operational error, a valve open during the purge, oil drainage, inappropriate hose (material), unprotected hose / pipe, contamination in a valve making it unable to close,

  - seals: poorly placed, inappropriate materials, old materials,

---

[45] Ammonia used as coolant (INTERNATIONAL INSTITUTE OF REFRIGERATION I.I.R. / I.I.R - 1993).

[46] Ammoniac, références et évaluation des risques pendant l'utilisation dans les installations de froid (AGA - FRIGOSCANDIA/ A. LINDBORG - 1994).

- poorly welded joints: inappropriate material in the pipes (excluding pressurised tank) which become fragile at low temperature,
- corrosion: only on the outside, rapidly detected during an inspection ("corrosion begins as a needle head and can smell bad for several days or weeks"?). The site is inspected and the component replaced,
- interior process error during installation start-up/shut-down and automatic reversion of defrosting with hot gas,
- combination of an interior modification of the process and another external defect described above.

The author states that the majority of leaks occur in gaseous form and can be controlled locally and that the pipes do not break directly, with the cracks or rips occurring as a consequence from an external physical influence. An orifice corresponding to approximately 20 or 30% of the diameter at the most occurs in all cases, which limits the volume of the leak in terms of time.

The failures described above are observed often. However, the accidents presented in this study required a more reticent approach. Numerous releases have occurred on the HP sections of installations and several sudden pipe ruptures have been reported (sections subjected to vibrations on a compressor outlet for example, external corrosion, etc.). The risk of a domino effect, and a tank or a pipe containing ammonia caught in a fire for example cannot be neglected. Finally, repair operations are not always as fast as planned (abandoned installations, employees present, insufficient understanding of the installation or work to be performed, etc.), thus leading to numerous interventions by outside emergency services.

b) Fire / explosion risk

Fires and explosions may concern the ammonia contained in refrigeration units and/or the related installations (coolers and their thermal insulation, in particular).

- Ammonia is considered a relatively poorly flammable gas[47] and does not seem to present an explosion risk in a closed environment[48/49]. Its explosive limits in air are between 15 and 28%. However, a study indicates that the L.E.L. may be reduced by 4% for an oil and ammonia aerosol (from a simultaneous lubricant leak). Furthermore, it is practically impossible to avoid the presence of decomposition hydrogen, thus forming in various areas[50]. Indeed, if pure ammonia in an inert environment decomposes beginning at 200°C, its dissociation into nitrogen and hydrogen starts at 110 to 120°C in the presence of water and iron. Air and oil also contribute to this dissociation.

  It is doubtful that the presence of air (between 75 and 97% in volume at atmospheric pressure) in a unit in operation, or that just combustion of lubrication oil, without any other favourable circumstance, can result in the combustion and explosion of the ammonia. However, it should be noted that the explosive limit and atomic hydrogen are between 4.1 and 75%. In these conditions, it is probable that suspicious cases of ammonia unit explosions were actually hydrogen explosions resulting in fires during which secondary ammonia explosions could have occurred, the major part of the ammonia having been burned up without explosion[52].

  All that was mentioned above, justifies the need:

  - for good dehydration of ammonia compression circuits (which does not always appear to be conducted as well as possible) even if traces of water do not lead to a major corrosion risk,
  - to avoid the use of nickel (a very active catalyst) in ammonia circuits,
  - to correctly monitor the pressures and to purge incondensable elements as soon as their presence is detected (the presence of continuous dehydrators is to be given special weight),
  - to regularly purge the oil without forgetting that which is present in the evaporators even in difficult cases (freezing installations),
  - to use on site welding, during possible repair, only with care and only if nitrogen (or another neutral gas) can be circulated in the

---

[47] Material Safety Data Sheet No. 16 (I.N.R.S.)

[48] "Les explosifs occasionnels", *Occasional explosives* (Lavoisier TEC&DOC/ Louis MEDARD - 1987).

[49] "L'ammoniac", *Ammonia* / Collection Enviroguide (Environnement Canada - 1985).

[50] "Réfrigération industrielle" (*Industrial refrigeration*) (EYROLLES / Jean-Georges CONAN - 1988).

location of the weld; the material must be sufficiently cooled on each side of the weld,

- to use only low voltage current to supply the safety and checking equipment in contact with the fluid.

- The thermal insulation used in buildings (coolers, etc.) often implements materials such as panels made of polyurethane foam sandwiched between 2 metal (aluminium) or plastic (polyester) sheets. Aware of the panels' vulnerability to fire, manufacturers offer other solutions[51]:
  - polyurethane foams impregnated with a flame retardant product, but its efficiency retention over time remains to be proven,
  - rock wool panels. The behaviour of this recent material, when subjected to the humidity of condensation inside the panel, is still not well known.

Statistics from the I.A.R.D. insurers association of the F.R.G. highlighted nearly 50 fires which irrupted in coolers or refrigeration warehouses between 1966 and 1977. With the exception of 2 acts of malicious mischief, these fires were primarily caused by failures in the installation or the electrical equipment (especially around door frames or cable feedthroughs in isolated walls), as well as weld or oxycutting. One case of carelessness is also reported following the defrosting of a cooler evaporator using an open flame[52]. Except for this last case, the causes of the accident remain identical in numerous accidents considered in this research study.

[51] Magazine FACE AU RISQUE No. 303 (R. DOSNE - May 1994).

[52] Fire prevention and safety in cold stores
(A.E.E.F. / I.I.R. Commisssion D11 - 1982).

Consequences

Excluding property damage and accidents which occurred during the dismantling of abandoned installations, the cases studied only rarely had consequences outside the establishments. No deaths among the general public were reported. A Swedish study[53] conducted based on several refrigeration accident reports also showed that no one died or was injured at a distance greater than 150 or 200 m from the ammonia leak. This study also indicates that if the ammonia forms a white cloud in a closed environment, the poor visibility indicates that the concentration is greater than 4%; acceptable visibility means that the combustion limit has not been reached.

Naturally, the danger studies must clearly state, on a case by case basis and based on several scenarios, the geographical limit distances of fatal effects and irreversible effects [54]. However, the distance of 150 to 200 m is equivalent to that generally formulated by default for installations (warehouses, etc.) presenting a fire risk (excluding BLEVE). This distance is sufficient to limit the thermal flux at a supportable level and to ensure emergency intervention in good conditions. It also seems to be consistent with the consequences observed in the 135 refrigeration accidents studied, such as the deadly effect limit. Furthermore, the limit of irreversible effects which must be confirmed, should be between 300 and 500 m (none of the accidents studied lead to an irreversible effect at that distance).

Evolution perspectives

This study has already indicated that for a refrigeration installation, the mass of ammonia over the installed power ratio is in the order of 5.5 kg of NH_3/kW. In light of a warehouse's storage volume, an approximate ratio of 0.097 kg/m^3 (without freezing) or 0.150 kg/m^3 (rooms with freezing capacity) can also be used[55]. The development of techniques, however, tends to reduce the quantity of ammonia used by reducing the diameter of the tubes and increasing the power and speed of the compressors[56].

---

[53] Ammoniac, références et évaluation des risques pendant l'utilisation dans les installations de froid,
Ammonia, reference and risk evaluation during use in refrigeration installations
(AGA - FRIGOSCANDIA/ A. LINDBORG - 1994).

[54] Guide de la maîtrise de l'urbanisme autour des sites industriels à hauts risques
(*Guide for the control of urbanisation around high risk industrial sites)* (French Ministry of the Environment - 1990).

[55] S.E.I. meeting / Profession of July 27, 1993 (meetings of August 4, 1993).

[56] Ammonia used as coolant (INTERNATIONAL INSTITUTE OF REFRIGERATION I.I.R. / I.I.R - 1993).

Alternative technologies in the refrigeration industry are summarised in Appendix 2 [57]. Technical developments are also to be foreseen in the design of current installations, especially if the use of ammonia in the refrigeration industry develops.

By increasing the thermal efficiency, these developments should allow the size of equipment and the ammonia load of installations to be reduced. Research should especially concentrate on the materials and lubrication oils as well as on compressor design, dimensioning and the optimisation of exchangers [58].

The fabrication based on series used for the R22 of small compressors, initially of open or rotary helical-screw type, which can be used with ammonia, should also not pose a problem[59]. Following laboratory studies, many improvements have been made over the last few years in terms of exchanger performance characteristics after modification of the geometry of the internal and external surface of the tubes used in the condensers and the evaporators of halogenated fluids. However, it remains to be proven that this equipment can be used with ammonia [60/61].

The development of techniques using an intermediate fluid (indirect cooling systems) is also heading in this direction and could possibly lead to limiting the storage and circulation of ammonia inside equipment located in machine rooms. The liquid coolers work well for storing refrigeration energy in the form of ice or eutectic salts. In this manner, they contribute to the thermodynamic recovery of the irreversibility brought about by the use of an intermediate fluid[60/62]. Hermetic chambers such as ageing rooms (bananas, tomatoes, etc.), controlled atmosphere storage rooms (also fruit packing houses and whose number increases regularly[63]), in which C.F.C.s were once selected in a direct expansion system, as well as facilities where the temperature is above 2°C, are also well-adapted to the use of intermediate fluid systems[58].

---

57 12 technologies pour l'avenir de l'environnement (*12 technologies for the future of the environment*)(Ministère de l'Industrie et du Commerce Extérieur / SRI International - 1992).

58 Machines frigorifiques / Développements futurs / Centre de thermique (*Refrigerating machines / Future developments / Thermal centre*), URA CNRS 1372,
INSA - Villeurbanne (Pr. M. LALLEMAND / RPF No. 766 - January 1993).

59 Nouveaux débouchés pour l'ammoniac (*New opportunities for ammonia*) (R.G.F. G. VRINAT -1993).

60 Club Ammoniac - GV of October 20, 1993.

61 Thermal Performance of Advanced Heat Exchangers for Ammonia Refrigeration System /
C.B. PANCHAL & T.J. RABAS (Heat Transfer Engineering, vol. 14 No. 4 1993).

62 Le stockage d'énergie frigorifique par mélanges eutectiques (*The storage of refrigeration energy by eutectic mixtures*) (SOTRAGAL / P. LE -
AITF Interclima - January 1991).

63 L'entreposage frigorifique français en chiffres, (*French cold storage in numbers)* - F. / F. BILLIARD & G. PIERSON - 1992).

CONCLUSIONS

RECOMMENDATIONS

As it is toxic, ammonia must be implemented in reliable installations that are operated and regularly checked by competent personnel. As the risk of leak cannot be zero, the public in the surrounding area must be provided with adequate information.

Considering the diversity and the size of the facilities concerned, training of the internal or external personnel (subcontractors) is one of the key factors enabling maximum safety to be ensured from the design of a refrigeration installation to its dismantling.

- Apart from chemical-related problems, the inconveniences of ammonia's incompatibility with copper and its derivatives is based essentially on the fact that the majority of refrigeration technicians and installers have only worked with C.F.C.s and copper tubing over the last 50 years. Today, there is thus a lack of know-how and training regarding the welding of steel pipes and high-pressure tanks[64].
- The low miscibility of ammonia with the oils commonly used modifies installation design and operation[65]. Such installations also require more maintenance that installations operating with C.F.C.s and the personnel must undergo special training. This is why ammonia is currently used in high-power industrial installations.

The following recommendations are not comprehensive and numerous regulatory texts, standards and recommendations applicable to refrigeration installations exist[66]. These recommendations are extracted from proposals formulated by the profession[67] or conclusions of specialised workgroups[68]. Some can be applied to all refrigeration

---

[64] SAVE summer training program - Club M3E (Association Française du Froid /A.F.F. G. VRINAT - 1994).

[65] Ammonia used as coolant (INTERNATIONAL INSTITUTE OF REFRIGERATION I.I.R. / I.I.R - 1993).

[66] Appendix 6: a few regulatory texts, standards and recommendations applicable to refrigeration installations.

[67] Charte des mesures à prendre concernant la conception, l'étude, la maintenance des installations de froid et de climatisation et la formation des personnels (annexe à la convention Pouvoirs Publics et professions du froid et de la climatisation - February 1989).

[68] Application of the OPAM ("ordonnance sur les accidents majeurs", *major hazards ordinance*) and conclusions drawn from hazard reports written for artificial ice skating rinks / Report of the "Sécurité des patinoires artificielles" (*Safety of artificial ice rinks*) working group (Federal Swiss Office of the Environment, Forests and Landscape - Installation Security Section - December 1991).

installations regardless of their use or the refrigerant used; they thus concern refrigeration installations using ammonia.

Installation design, construction and commissioning

Refrigeration installations must only be built and installed by qualified manufacturers. The components, equipment and consumables (oils, heat transfer fluids, etc.) must correspond to the operating conditions.

Toxic Risk

1. The study of components, the selection of materials and equipment, the design and the construction of the installations (volumes of equipment and tanks, etc.) must allow a refrigerant load that is as small as possible and to reduce product leaks to a minimum.

Whenever practical, the refrigerant load must be reduced by using an indirect refrigeration system using a secondary fluid (water, glycol, brine, etc.). The ammonia load can also be limited to the machine room in certain cases.

2. The installation must be divided into sections which can be isolated. If the tanks are not so equipped, each section must be equipped with correctly sized connection in order to connect a recovery unit. Installations must be able to isolated both locally and remotely.

The installation's elements (compressors, equipment, piping, etc.) for which maintenance requires that they be opened (replacement of filters, oil changes, etc.) must be equipped with their own shut-off system and be equipped with transfer valves when they cannot be connected to the vacuum system.

3. In public installations, such as ice skating rinks, partitions placed between the machine room and the other rooms must prevent the toxic gas from spreading. As for fire-stop compartments, the openings in the conduit duct in the direction of public facilities must be plugged. The ducts running alongside parts of the installation that are accessible to the public must be confined. Ammonia detectors, connected to the general gas alarm system, must be installed in the ducts.

In addition, the drains in the floor of the machine room, the drain holes in the conduit ducts, in the pumping pits, etc. must be plugged to prevent ammonia from being released into the sewer system.

4. The pipes which convey the refrigerant must be as short as possible. The pipes located on the outside of buildings should be confined whenever practical. The atmosphere trapped in the double pipe system must be able to be checked continuously (scanning with an inert gas, ammonia detectors).

The installation and the anchoring of the hoses must be performed carefully.

Assemblies must be made without stress to avoid cracking the metal.

5. The return lines in pump-fed circulating systems must be installed with a continuous slope toward the separator.

6. The vibrations induced by motorised equipment deteriorate the pipes and can lead to refrigerant leaks. The compressors create pulsing of the gaseous column and/or mechanical vibrations. The drive motor can also induce such effects. These vibrations depend on:

- the dimensioning of the foundations,
- the dimensioning of the pipes,
- the layout and the fastening of the pipes,
- the selection and the adjustment of control devices.

In the sections of pipe concerned, special attention must be given to the welding of pipe connections and assemblies, in relation to threaded, flange or crimped fittings.

Compressors and their drive units must be perfectly aligned.

Before commissioning the installation, an operational test must be conducted to analyse the vibratory behaviour of the various components. If required, measures shall be taken to limit the amplitude of the oscillations to the recommended values. Inserting dampers or equivalent devices can attenuate the pulses in the intake and discharge lines. In certain special cases, an amplitude limiter for the oscillations can also be inserted.

7. Overpressure protection must be of "double inversion safety valve" type.

8. Manual shut-off valves must be "counter-seat" type to allow valve heads and seals to be changed without a refrigerant leak. Stuffing box type valves must be "bellows" or "diaphragm" type or be equipped with a gastight cap.

9. The purges installed on the installations (compressors, etc.) must be collected.

Generally speaking, connections opening to the open air and not used during normal operation, as well as the purge or filling tubes, must be plugged by a pressure-resistant device.

10. The poorly controlled injection of liquid refrigerant into vapour pipes is to be avoided (risk of overpressure).

11. There must be a sufficient number of footwalks, stairs or ladders to ensure the correct operation and verification of the installation. The use of pipes or their securing components as a step is prohibited.

12. A refrigerant recovery unit must be permanently available on sites equipped with a refrigeration installation normally containing a dischargable load of refrigerant greater than 500 kg.

13. The installation must only be charged with the quantity of refrigerant specified.

14. Equipment verification, leak tests and installation commissioning can only be performed by trained and qualified installer personnel, possibly under the control of an independent inspector.

The installation must be subjected to a leak test at the end of the assembly phase, either globally or by section and sub-assembly. This test shall be certified in writing. The test must be repeated if the installation is modified or remains out of service for more than 6 months.

During installation commissioning, all control and safety devices must be checked under normal operating conditions. The inspection shall be performed according to a "checklist". Safety devices shall be protected against unauthorised intervention (sealed, etc.).

15. When installations are delivered assembled to the site, the user must be informed of the function and the operation of the installation, of the sort of risks presented by the refrigerant used as well as the consequences of a possible leak of this refrigerant. Qualified personnel shall instruct the user how to detect leaks and the measures to take in an emergency situation.

The refrigerant transfer methods inside the installation must be represented on a flow diagram and explained in the operating instructions. A copy of these documents shall be available and placed in a visible manner near the installations on a permanent basis.

16. The rooms containing ammonia, accessible only to authorised individuals, shall be indicated on a general room closing drawing.

17. The user shall be informed of his/her responsibility regarding the elimination of the refrigerant, refrigeration oils and components of the system polluted during normal operation of the installation or when it is decommissioned.

Fire risk [69]

18. Interrupting the continuity of the combustible part of the materials between panels is an important factor. This objective is achieved by offsetting a combustible wall by one or two lengths of non-combustible panels.

[69] Magazine FACE AU RISQUE No. 303 (R. DOSNE - May 1994).

Compartmentation and the separation of activities are another solution (receiving and storage of raw materials, manufacturing workshops, packing and packaging, refrigerated storage, etc.).

The installations can be equipped with fire detection equipment. Owing to the presence of smoke, ionic detectors can be more sensitive than differential heat detecting devices. In locations where frost is likely to form, these detectors can be equipped with a 6 to 10 W electric heating element powered by 24 to 30 VDC [70].

When unavoidable, the openings of belt conveyors between insulated sections can be protected by sprinklers. These devices, however, are not always reliable at low temperatures (frost, etc.) or efficient against burning insulation. Installations using carbon dioxide are not widespread due to their high operating cost (1,000 m^3 of air requires approximately 1,650 kg of CO_2). The primary extinguishing product remains water. In Germany, technical rules require reference values which can reach 192 m^3/h for commercial and industrial buildings. For 50,000 m^3 of cooler space, by using 2 fire hydrants, an output of at least equal to 120 m^3/h at 4 bar for 2 hours must be guaranteed; no location inside the warehouse must be located more than 80 m from the nearest fire hydrant[72].

The auxiliary buildings, administrative and social buildings, laboratories, and power plants can be located a distance away from the body of the plant and placed according to the prevailing wind. This provision also has the advantage of reducing the risk of a domino effect (ammonia tank engulfed in the fire, etc.).

The rooms used as fire-stop compartments (machine room, etc.) must be fitted with automatic doors. Pipe and cable feedthoughs in the walls must be blocked with a fire resistant material.

19. In Germany, and according to current knowledge, the use of flammable insulating materials[71] limits the volume of a fire-stop space to a maximum of 24,000 m^3. The firewalls which surround it must consist of non-flammable materials able to efficiently resist the spread of fire for at least 90 min. These walls must sufficiently extend past the roof of the fire-stop area in order to constitute an obstacle to the spread of fire (wind, storm, etc.) on the neighbouring parts of the building[72].

The fire-stop space volume may be increased to 48,000 m^3 when non-flammable materials or an external insulation are used. Apart from warehouses equipped with raised shelving which are subject to other prevention criteria, the working height of the coolers must not exceed 14.5 m.

20. Electrical installations represent a weak link in an environment of flammable foam. Building insulation implicates the use of false ceilings and volumes under the roof that are used to route numerous cables in an environment where the foam can be

---

[70] Prévention des incendies et sécurité dans les entrepôts frigorifiques, *Prevention of fire and safety in refrigeration warehouses* / Science et Technique du froid/ Association Européenne des exploitations Frigorifiques (Institut International du Froid/ Commission D11 - PARIS - 1982-2).

[71] As per category B defined in standard DIN 4102.

bare. Regular inspections using thermography allow sensitive points of the installation to be detected by infrared (conductor of insufficient diameter, etc.).

Furthermore, in electrical heating installations (de-icing, defrosting, etc.), the surface temperatures retained must not be hazardous[72].

21. Reinforced preventive measures and information directed to intervening parties are necessary during maintenance/servicing operations (no smoking, fire permit, etc.).

Operation, repair and inspections

Refrigeration installations must be thoroughly inspected and maintained on a regular basis and repaired by specialised personnel who have received the appropriate training. Routine checks can be performed by properly trained personnel[72].

The work performed must be recorded. In all cases, the user must receive a copy of the inspection report or the work record sheet.

[72] Charte des mesures à prendre concernant la conception, l'étude, la maintenance des installations de froid et de climatisation et la formation des personnels, *Charter of measures to take relative to the design, study, maintenance of refrigeration and air-conditioning installations and personnel training* (Appendix to the Public Authority and Refrigeration and Air-Conditioning Professions convention - February 1989).

22. Agents must be identified with their respective duties and functions in a written document clearly stating the responsibilities for:

- the safety of the installation,
- the condition of the installation,
- the prevention of accidents (qualified personnel must be available 24h/7).

Specifications must be established for the safety officer and for his/her alternate.

23. Operating and maintenance instructions shall be established according to standards of the NF 35 400 series relative to safety requirements for the design, the equipment, the installation and the operation of refrigeration installations.

24. The frequency of the checks and required maintenance depends on the type and the intensity of the installation's operation as well as the refrigerant load.

Every quarter if possible, or, failing that, once per year, the refrigeration installations must undergo periodic maintenance with at least a refrigerant leak test.

The checks will focus especially on the installation's safety-related elements (tanks containing ammonia, safety valves, shut-off valves, emergency tripping systems, alarm equipment, etc.) and on the other critical parts (condensers, manifolds, etc.).

The miscellaneous checks and inspections shall be carefully planed, with certain checks being conducted only when the installation is shut down. Furthermore, maintenance plans shall be established for the entire installation; the latter shall include, as required, any possible maintenance contracts.

25. All leak detected must be repaired immediately. For leak elimination, the part of the circuit concerned must be isolated and the refrigerant that it contains must be transferred to the rest of the circuit or into a recipient reserved for this purpose.

26. Maintenance operations shall include a condition check, operational check and monitoring of the adjustment of the safety systems and devices.

27. Repair operations requiring assistance of other trades (welders, electricians, etc.) shall be conducted according to the instructions of a refrigeration specialist.

28. In order to reduce releases, the refrigerant and the oil must be pumped while minimising losses. Pressurised refrigerant must not be purged to the open air. Wastes must be eliminated with respect to current regulations.

29. Machine rooms must not be used for other operations (drying clothes, workshop, warehouse, etc.). This restriction particularly concerns the storage of flammable, combustible or explosible substances.

Training of contractors[73/74]

30. The qualified personnel installing, repairing or maintaining the refrigeration installation must be trained in compliance with the legislation governing hygiene and safety. Personnel must have sufficient experience and knowledge, particularly concerning pressurised recipients and the physical, chemical and toxicological characteristics of ammonia and its aqueous solutions. In addition, personnel must have the ability and the sense of accountability required to perform reliable work. This involves:

- a solid understanding of the field of refrigeration,
- familiarisation with the corresponding legislation, labour code and recognised trade practices,
- an ability to evaluate the correct operation and safety of a refrigeration installation.

31. The individual who performs and/or monitors the assembly, repair and maintenance must have undergone certified "refrigeration technician" training or follow-up training on the basics of the principles discussed above. In addition, the individual must have sufficient practical knowledge and solid experience in operating this type of installation.

32. Qualified personnel must undergo continuous training relative to the new or existing developments and innovations in the field of refrigeration or the handling of refrigerants, related materials and consumables.

33. Adapted written operating instructions shall be provided at each installation. Information in case of an incident or accident shall be clearly formulated.

Intervention / Evacuation

---

[73] Charte des mesures à prendre concernant la conception, l'étude, la maintenance des installations de froid et de climatisation et la formation des personnels, *Charter of measures to take relative to the design, study, maintenance of refrigeration and air-conditioning installations and personnel training* (Appendix to the Public Authority and Refrigeration and Air-Conditioning Professions convention - February 1989).

[74] Application of the OPAM ("ordonnance sur les accidents majeurs", *major hazards ordinance*) and conclusions drawn from hazard reports written for artificial ice skating rinks / Report of the "Sécurité des patinoires artificielles" (*Safety of artificial ice rinks*) working group (Federal Swiss Office of the Environment, Forests and Landscape - Installation Security Section - December 1991).

34. An alarm and intervention plan (internal contingency plan, etc.) in case of an accident shall be established, in collaboration with the emergency response and rescue services, and disclosed to all personnel, including any casual employees. Exercises shall be conducted with the emergency response services on a yearly basis. The loudspeaker messages must be prepared (recorded).

The surrounding population and the local media must be informed. The measures required for the vicinity must be taken (telephone numbers for the fire brigade, police, local radio station, etc.).

35. The operator of the installation and the external companies likely to respond must have the appropriate equipment:

- adapted tooling,
- specific professional equipment for loading and transferring refrigerant (including the recovery and neutralisation of fluids),
- leak testing and inspection equipment,
- inspection and measurement instruments,
- operating and related products,
- documentation.

36. The access roads and paths must be marked and free of obstacles to allow a clear passageway at all times. Anyone should be able to open the doors from the inside.

Emergency lighting must be available at all times (automatic recharge, etc.). The emergency power unit must also supply the speakers, if installed.

These provisions must especially be respected for public buildings.

37. Emergency switches must be installed on the outside of the machine rooms. The personnel must have easy access to their location and be instructed as to their operation.

The position of these switches and all control devices which, in case of an accident, are important for the safety of the operation must be identified on a diagram or on the installation itself (colour, etc.). A copy of the diagram shall be displayed in the machine room and a second copy shall be easily accessible outside the room.

38. A wind direction indicator (flag, etc.) shall be installed in a location that is clearly visible both during the day and night.