fertilizers europe

GUIDANCE FOR INSPECTION OF AND LEAK DETECTION IN LIQUID AMMONIA PIPELINES

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Contents

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1. SCOPE

This document produced by Fertilizers Europe provides guidance for the inspection of and leak detection in liquid ammonia pipelines.

The guidance focuses on pipelines transporting cold (close to the atmospheric boiling temperature of -33°C) or warm liquid ammonia, with a diameter of at least 75 mm. It deals with above-ground and underground (also called buried) pipelines which are located outside battery limits i.e. not inside ammonia or inside downstream plants but between ammonia plant and harbour, tank storage, other plants or between sites. Thus, the guidance covers off-site pipelines and certain on-site pipelines, as defined above.

Practices of design, inspection and leak detection with respect to liquid ammonia pipelines are not uniform within the European Union (EU). They differ from Member State to Member State. This guidance provides an overview.

The guidance is based on inspection and leak detection practices of various experienced liquid ammonia pipeline operators in the EU. It does not cover fabrication inspection. The underlying intention is to maximise the operational safety and reliability of these pipelines and to reduce environmental and health risks.

2. INTRODUCTION

This document has been produced by Fertilizers Europe to provide guidance for the safe operation, inspection and leak detection concerning liquid ammonia pipelines. It also covers the associated provision of emergency systems. This guidance is one of a series of guidance documents, which Fertilizers Europe has produced and published for the benefit of its members. These cover hazardous properties of ammonia [Ref 15], ammonia rail transport [Ref 9] and inspection of atmospheric, refrigerated ammonia storage tanks [Ref 12].

Ammonia is produced in large quantities, with typical plant capacities being in excess of 1000 tonnes/day, which need to be transferred or transported to the user plants such as nitric acid, ammonium nitrate, urea and other chemical plants. Much of this transfer between sites as well as within integrated complexes takes place by pipelines. In a significant number of cases these pipelines are close to public roads or other areas of population, and also there have been a number of accidents with such pipelines (mostly outside the EU region). Therefore, safety related to these pipelines is particularly important.

The Fertilizers Europe Task Force set up to prepare this guidance, first carried out a literature survey to check if any guidance was published on this topic and what kind of accidents had taken place in order to assess the required scope of the intended guidance and the background work which might be required. Following this initial search, it was decided to carry out a survey of the pipelines owned or operated by its Fertilizers Europe members by way of a questionnaire. It covered various relevant aspects such as location, size parameters, operating conditions, nature of run (above-ground or buried), materials of construction, provision of protection against corrosion and physical damage, thermal relief protection, inspection regime, provision of ammonia leak detection systems and emergency isolation facilities.

The findings of this survey and other published data were used to develop this guidance. The main findings of the survey about the existing pipelines are summarised in Section 3. An overview of the relevant ammonia properties is given in Section 4.

Section 5 deals with incidents and brings out key learning points. Specific areas of concern, inspection aspects and leak detection methods are described in Sections 6, 7 and 8. Finally, mitigation and emergency response issues are covered in Section 9.

3. SURVEY OF EXISTING PIPELINES

Transport of large volumes of liquid ammonia by pipeline over great distances is far more economical than by river barge or rail [Ref 1, 2, 3, 4]. Very large pipeline systems can be found in the USA and Russia/Ukraine.

Fertilizers Europe carried out a literature search as well as a survey of pipelines operated by its members. Results of these are summarised below by region.

3.1. USA

Pipelines carrying liquid ammonia have been operating reliably for decades in the United States. Some 5000 kilometres of mild carbon steel pipeline are in operation there and have a delivery capacity of about 2 million tons of ammonia per year. Main branches have diameters of 200 and 250 mm. These pipelines are generally underground and experience essentially no internal corrosion. Main pipeline systems are:

- **Gulf Central**. The 3057 km Gulf Central pipeline is the longest system and connects the major producers along the Texas and Louisiana Gulf coast with terminals in Arkansas, Iowa, Illinois, Indiana, Nebraska and Missouri.
- **MAPCO**. The MidAmerica Pipeline System (MAPCO) extends from Northern Texas, across Oklahoma, Kansas, Nebraska and Iowa, and ends in Minnesota, all intensive agricultural areas. The total length is 1754 km.
- **Tampa**. Another shorter system (132 km) is the Tampa Bay pipeline in Florida.

3.2. Russia/Ukraine

A long ammonia pipeline has been in operation since 1983 in Russia/Ukraine. It connects the large production facilities Togliatti/Gordlovska in Russia with the Black Sea port of Odessa in the Ukraine. Total length is 2424 km, of which 1400 km cross Russian territory and more than 1000 km cross Ukrainian territory [Ref 5, 6]. Reportedly, the diameter of the line is 350 mm.

3.3. EU

Pipeline transport of liquid ammonia in the European Union is not as significant a factor as in the US and in Russia/Ukraine. Only relatively short pipeline systems are in operation. An overview is presented in Table 1.

Table 1 LIQUID AMMONIA PIPELINES IN THE EU

Location	Distribution function	Above-/ underground	Length (km)	Operating pressure (barg)	Operating temperature (°C)	Diameter (mm)	Capacity (tpd)
Belgium							
Pipeline 1	To onsite customers	Above	10	22	10-15	100 and 150	3100
Pipeline 2	To offsite customers	Under	12	22	10-15	100 and 150	3100
Germany							
Pipeline 1	To onsite customers	Above	24	21	5-40	50-200	2600
Pipeline 2	Harbour to storage	Above	2.8	11	5-40	150	1900
Pipeline 3	To offsite customers	Under	12	10-15	1-5	275	3600
Italy							
Pipeline 1	To offsite customers	Under	74	17	10	200	900
Netherlands							
Pipeline 1	To onsite customers	Above	5.8	16	5	100-200	3000
Pipeline 2	Harbour to storage	Above	1.0	10	-32	80	1000
Poland							
Pipeline 1	Plant to storage	Above	1.2	10-15	-30	200	1500
Pipeline 2	Storage to plant	Above	1.5	13	-7 to 0	75, 100, 150	120
Pipeline 3	Storage to harbour	Above	6.0	8-13	-33 to -15	350	14000
Pipeline 4	Storage to harbour	Above	5.9	8-13	-33 to -15	100	600
Pipeline 5	Plant to storage	Above	1.2	5-22	-5	150	1680
Portugal							
Pipeline 1	Plant to harbour	Above	1.9	13	-30	100	900
Spain							
Pipeline 1	To offsite customers	65% Under	10	14.5	13	150 and 350	860
Pipeline 2	Harbour to tank	95% Above	1.5	3.5-4.5	-33	300	10000
Pipeline 3	Harbour to tank	90% Under	2.4	6	-33	300	12000
Pipeline 4	Tank to plant	Above	4.2	15-18	8-15	100	390
U.K.							
Pipeline 1	Harbour to storage	Above	8.8	30	-32	100 and 150	240
Pipeline 2	Harbour to plant	Above	6.9	21	-33 to +25	150	1440
Pipeline 3	Plant to Harbour	Above	6.8	21	-28	150	1440
Pipeline 4	To offsite customers	Above	2.2	14	-29 to ambient	100	290
Pipeline 5	To offsite customers	Above	1.6	14	-29 to ambient	100	240
Pipeline 6	Harbour to storage	Above	2.0	2-5	-32	300	12000
Pipeline 7	Harbour to storage	Above	2.0	2-5	-32	75	600

Note 1: Only pipelines with a length of 1 km or more have been listed.
Note2: The following pipelines are now out of operation:

- *Carling (France) to Besch (Germany), was first commissioned mid last century.*
- *Most to Lovosice (Czech Republic), was first commissioned early 1960's.*
- *Cabo Ruivo to Alverca (Portugal), was first commissioned in 1960s.*
- *Grand Quevilly to Oissel (France), was first commissioned in 1967.*

3.4. Other parts of the world

Fertilizers Europe has not carried out a survey of liquid ammonia pipelines in other parts of the world.

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4. PROPERTIES OF AMMONIA

4.1. General characteristics

Chemical formula	NH_3
Molecular weight	17.03

At ambient temperature and atmospheric pressure, ammonia vapour is an alkaline colourless gas with a pungent and suffocating odour. Ammonia gas is very soluble in water. The gas is strongly irritant/corrosive to the skin, eyes and respiratory tract and has toxic properties. Ammonia gas condenses into a colourless liquid ("liquid ammonia" or "anhydrous ammonia") when cooled and compressed [Ref 9].
CAS Registry number is 7664-41-7, EINECS number is 231-635-3, EINECS name is Anhydrous Ammonia [Ref 9, 10].

4.2. Physical properties

The Table below summarises a number of common physical data [Ref 9, 10,]:

		Liquid	Gas
1	Density (0°C, 101.3 kPa)	638.6 kg/m³	0.7714 kg/m³
2	Density (-33.43°C, 101.3 kPa)	682 kg/m³	0.888 kg/m³
3	Relative vapour density		0.6 (air = 1)
4	Boiling point (101.3 kPa)	-33.43°C	
5	Melting point	-77.71°C	
6	Critical temperature	132.4°C	
7	Specific heat (10°C, 1MPa)	4.67 kJ/kg.K	
8	Heat of vaporisation (101.3 kPa)	1370 kJ/kg	
9	Heat of solution (1:1 mol H_2O, 0°C)	30.69 kJ/mol NH_3	
10	Solubility in water (10°C)	40.0 wt% NH_3	
11	Solubility in water (50°C)	18.5 wt% NH_3	
12	Flammability limits (0°C, 101.3 kPa)		16-27 vol% NH_3 in air

4.3. Vapour pressure

The vapour pressure of boiling ammonia [Ref 11] as a function of temperature is:

Temperature (°C)	Pressure (bar)
-74.3	0.08
-33.6	1.01
-18.7	1.96
4.7	4.9
25.7	9.8
35.0	12.8
50.1	19.6
66.1	29.4
78.9	39.2

Many more physical properties can be found in [Ref 9], [Ref 10] and [Ref 15]. Much more physical properties have been listed in [Ref 1]. A useful nomogram with properties of ammonia is shown in Appendix 4.

4.4. Chemical properties

Ammonia is an alkaline gas. The pH of a 1% aqueous solution is approximately 11.7. Ammonia in contact with certain other chemicals including mercury, chlorine, iodine, bromine, calcium, silver oxide or hypochlorites can form explosive compounds. Gaseous ammonia can react violently with nitrogen oxides and strong acids. Ammonia is very corrosive to copper and copper containing alloys. Equipment in contact with ammonia should therefore not contain this element [Ref 9].

4.5. Health hazards

Ammonia is a potentially hazardous substance, although it occurs naturally as a result of many biological processes. It can produce acute effects on humans and animals. Ammonia has strong alkaline and hygroscopic properties, which cause irritation or corrosion to damp tissue surfaces such as the eyes, respiratory system and skin.

Ammonia has a pungent odour; the odour threshold of ammonia is in the region of 5 ppm. Concentrations between 20 and 50 ppm are detectable by most people. This provides an adequate warning of its presence well below the hazardous concentration levels.

Gaseous ammonia affects the mucous membranes and the respiratory tract and severely irritates the eyes. Inhaling high concentrations may cause pulmonary oedema. High gas concentrations in the air may also cause blisters and chemical burns on the skin. The effects of exposure to various vapour concentrations are summarised in Table 2 [Ref 19].

Table 2 EFFECT OF EXPOSURE TO AMMONIA

Vapour Concentration ppm v/v	General effect	Exposure period
5	Odour detectable by some people	-
25	-	Occupational exposure standard-long term, 8hr/TWA (MAC value in many countries)
35	-	Occupation exposure standard-short term, 15min/TWA
50-100	Irritation detectable by most people.	Tolerable for people unaccustomed to exposure for up to 2 hours. People accustomed to exposure can tolerate higher concentration over the same period
400-700	Immediate eye, nose and throat irritation	½ -1 hr exposure causes no serious damage although upper respiratory tract irritation may persist for 24hr following 30min exposure. Aggravation of existing respiratory problems could occur.
1000-2000	Severe coughing, severe eye, nose and throat irritation.	Damage to eyes and respiratory system can result in minutes if not treated quickly. 30min exposure can produce very serious effects in people predisposed to severe respiratory problems.
3000-4000	Severe coughing, severe eye, nose and throat irritation.	Can be fatal after 30min. Estimated LC_{50} (derived from animal data) for 2hr exposure in this region.
5000-12000	Respiratory spasm. Rapid asphyxia.	Fatal within minutes. Estimated LC_{50} (derived from animal data) for 30min exposure in this region.

Liquid ammonia in direct contact with the skin freezes tissues on contact and causes chemical burns.
Indicative Occupational Exposure Limit Values (IOELV) of ammonia, anhydrous, are:

- *Short Term Exposure Limits (STEL 15 min.): 50 ppm = 36 mg/m^3*
- *Time Weighted Average (TWA 8 hours): 20 ppm = 14 mg/m^3*

4.6. Fire hazard

Ammonia gas is combustible, but it is very difficult to ignite. Minimum auto-ignition temperature according to DIN 51749 is 651°C, and the auto-ignition temperature of ammonia in contact with hot steel is about 650°C as well [Ref 9]. Furthermore, ammonia has a very high ignition energy.

Experiments as well as observations during accidents have shown that in the case of a release of ammonia in the open air, the ammonia-air mixture is generally outside the flammability limits mentioned under “Physical properties” above. Therefore, the risk of a fire or explosion from an ammonia-air mixture outside buildings tends to be negligible. On the other hand, in confined spaces, the situation can be different and the risk of explosion should not be ignored.

In EU and UN legislation ammonia is not classified as a flammable gas [Ref 9]. In the UN transport classification system ammonia is classified as Division 2.3 *Toxic gases*; with a subsidiary risk of class 8 *Corrosive Substances* and special provision 23, which states ‘’*Even though this substance has a flammability hazard, it only exhibits such hazard under extreme fire conditions in confined areas*’’. In the EU system classification of ammonia is denoted by symbols T (Toxic) and N (Dangerous for the Environment); its flammable hazard is identified by the risk phrase R10 (flammable).

Under the forthcoming Globally Harmonised System (GHS) the above classification is likely to be retained with some variation; readers are advised to consult the latest regulations.

5. INCIDENTS WITH PIPELINES

5.1. Pipelines in general

The European Gas Pipeline Incident Data Group (EGIG) [Ref 20] provides statistical information on 1123 incidents with EU gas pipelines for the period 1970-2004. Causes of these incidents have been classified and are reported in Table 3. It is worth noting that almost half of these incidents are the result of external interference.

Table 3 CAUSE ANALYSES OF PIPELINE INCIDENTS IN EUROPE

Cause of incident	% of all incidents	Subdivision
External interference	49.8	Digging, piling, ground works, anchor, bulldozer, excavator, plough, protecting casing/sleeves
Construction defects / material failures	16.7	
Corrosion	15.1	
Ground movement	7.1	Dyke Break, erosion, flood, landslide, mining, river
Hot-tap made by error	4.6	
Other and unknown	6.7	Design error, lightning, maintenance
Total	100	

5.2. Liquid ammonia pipelines

Various incidents with liquid ammonia pipelines above 75 mm diameter have been identified in literature [Ref 7]. Most of these incidents took place in the USA, which is understandable as the US is home to vast liquid ammonia pipeline systems. These nine incidents are summarised below:

- **Texas City, Texas, 1969**. A 200 mm diameter liquid ammonia pipeline failed as a result of an unforeseen freeze-thaw cycle in the water containing annular space of a double walled ammonia pipe.
- **McPherson, Kansas, 1973**. A major leak developed in a 225 mm diameter liquid ammonia pipeline due to overpressure on a previously mechanically damaged pipe part.
- **Texas City, Texas, 1975**. A 150 mm diameter liquid ammonia pipeline ruptured due to external corrosion as a result of mechanical damage to the pipe coating and interference in the cathodic protection.
- **Ince, England, 1981**. A minor leak developed from a small branch of a 200 mm diameter liquid ammonia pipeline that was not in continuous operation. Root cause was external corrosion due to unforeseen (rain) water entry to the pipe surface
- **Algona, Iowa, 2001**. A large ammonia leak developed in a 200 mm diameter liquid ammonia pipeline as a result of maintenance work on a valve in that pipeline

- **Grand Parish, Louisiana, 2001**. An ammonia thief drilled into a valve of a large liquid ammonia pipeline, probably to obtain ammonia to make the drug methamphetamine.
- **Kingman, Kansas, 2004**. A huge leak developed after a rupture in a 200 mm diameter liquid ammonia pipeline. Probable cause was metal fatigue cracking in combination with previous mechanical pipe damage.
- **Clay County, Kansas, 2006**. A 200 mm diameter liquid ammonia pipeline failed. As far as we know, the cause has not been determined yet, but seam failure is suspected.
- **Mulberry, Florida, 2007**. The Tampa Bay liquid ammonia pipeline near Mulberry, possibly with a diameter of 100 mm or 150 mm there, developed a leak. A boy drilled a hole in the pipeline out of curiosity.

5.2.1. Consequences of these ammonia incidents

The largest ammonia escape in these incidents was probably the one in Kingman, Kansas, in 2004. Reports quote 200 000 gallons (760 m^3) of liquid ammonia loss. A picture of the cloud resulting from this incident, copied from [Ref 18], is shown in picture 1.

Picture 1. Large plume of escaping ammonia from the Kingman pipeline incident (2004).

The ammonia escaping as a result of these 9 incidents has not led to fatalities. One person had 18% of his body burnt by ammonia. Various persons were hospitalised, mainly with respiratory problems. Various roads were closed by the authorities, leading to traffic hindrance. Various land animals died. Hundreds of people were evacuated. In the Algona incident, some 1.3 million fish died, and the drinking water supply of a major US city was threatened.

5.2.2. Summary of basic causes of these ammonia incidents

Basic causes were overpressure (1x), external corrosion (2x), maintenance work (1x), metal fatigue cracking (1x), seam failure (1x) and an unforeseen freeze-thaw cycle (1x).

Moreover, two of the failures were the result of malicious acts. These two failures made clear that liquid ammonia pipelines could potentially be subject to terrorist attack [Ref 8].

None of these 9 incidents was the result of the classical mistake with agricultural or excavation equipment. The occurrence of excavation incidents can be minimised by the practice of installing sufficient line markers (see Section 6.3).

6. DESCRIPTION OF SPECIFIC AREAS OF CONCERN

6.1. Design codes and materials of construction

The European Pressure Equipment Directive [Ref 14] was issued in 1997. This is a Directive that applies to pressurised systems in general. Therefore, it covers the design of liquid ammonia piping as well, although it is not a Directive specific to liquid ammonia piping. However, most of the liquid ammonia pipelines in the EU were built before 1997, and the design practices differed from Member State to Member State. This resulted in the development of national design codes, some of which are listed in Appendix 1. Some of the requirements of the European Pressure Equipment Directive are addressed in these codes.

In most cases the material of construction is carbon steel. However, there is a tendency to go to stainless steel for its good corrosion resistance in this service when for example replacing parts of existing lines or constructing new short/small diameter pipelines. Consequently, the overall cost of maintenance (e.g. including sand/grit-blasting and painting, removal/re-installation of insulation) and inspection of a carbon steel pipeline can be higher than for a pipeline of stainless steel. Some examples of applied construction materials are shown in Appendix 2.

6.2. Other design requirements

In the USA, design requirements for transportation of hazardous liquids by pipeline are described in the US Code of Federal Regulations No. 49 (Transportation), part 195 (Transportations of hazardous liquids by pipeline) [Ref 13]. This is a general code, not specific for ammonia; however, ammonia is one of the chemicals belonging to the category "hazardous liquids".

In the EU, each national authority of a Member State determines its own design requirements for liquid ammonia pipelines (in addition to the design codes listed in Appendix 1). In some countries this is done via environmental permits. Added requirements can be related to widely differing items like line markers for identification, corrosion, thermal relief valve practice, etc. More detail is given in the following paragraphs.

6.3. Line markers and warning signs

Line markers are necessary for the identification of the pipeline and its management company, particularly where the line runs through public, rural or residential areas.

Special attention should be paid to line markers for underground pipelines; these line markers are an important warning sign to the public and also serve as a useful tool to limit pipeline damage by negligent excavation activities. However, in one EU country, the installation of line markers is reportedly not made prominent for security reasons.

Examples of typical line markers for different situations of pipelines are described below.

Above-ground onsite pipelines are usually provided with stickers at regular intervals. These show the product name and flow direction, and optionally a danger symbol and an onsite emergency telephone number. An example is shown in picture 2.

Picture 2. Marker on an above-ground onsite pipeline.

Above-ground offsite pipelines, running in areas accessible to the public, are generally labelled at regular intervals with line markers, for instance stickers, showing the product name (ammonia), the name of the operator and an emergency telephone number for the operator.

Underground offsite pipelines, running in areas accessible to the public, are generally provided at suitable intervals with line markers on poles directly above the track of the pipeline. Such markers are also placed at locations where the pipeline changes direction, thus providing a proper view of that track. This can minimise the risk of causing damage by agricultural or excavation equipment. Line markers can also be installed at locations where the pipeline crosses roads, railways or waterways. The line markers can display useful information such as a pole number, the product name (ammonia), the name of the operator and an emergency telephone number for the operator. An example is given in picture 3.

Picture 3 (left). Marker of an underground off-site pipeline.
(Company name and telephone number have been erased for reasons of privacy)
Picture 4 (bottom left). Roofed marker of an underground off-site pipeline.
Picture 5 (bottom right). Marker of an isolation valve station.
(Company name and telephone numbers have been erased for reasons of privacy)

When the pipeline is inspected from a helicopter, the visibility of the markers can be improved by equipping them with a roof. See picture 4.

Isolation valve stations of underground pipelines are located above ground. These isolation valve stations are to be fenced off to make them inaccessible to the public. Also, they are to be marked properly ("Ammonia pipeline; from/to; telephone number of the operator; emergency telephone number of the authorities; no admittance; danger"). An example is given in picture 5.

6.4. External corrosion and insulation

Above-ground carbon steel pipelines are generally coated/painted on the outside surface to protect against corrosion. This is sometimes also a requirement stipulated in the environmental permit. The coating usually consists of an epoxy paint in various layers. In addition to paint, a protective covering, such as Denso tape, may be used. It should be noted that lines with a variable temperature are potentially most susceptible to external corrosion; see also Section 6.15 “Ice formation”. Pipe parts made of stainless steel are often not coated; however, when the pipeline can be exposed to certain chemicals, such as chlorides in coastal areas, it can be necessary to coat the stainless steel pipe also.

Buried carbon steel pipelines must be coated to control external corrosion. Typical coatings are bituminous materials, (extruded) polyethylene and polyurethane. At the soil to air interface, buried carbon steel pipelines have corrosion issues similar to those of above-ground carbon steel pipelines. A pipe wrap should be utilised at that interface to prevent external corrosion.

Insulation is applied where required (see also Section 6.15 “Ice formation”). Moisture in and under insulation may cause external corrosion of carbon steel pipelines.

6.5. External corrosion under pipe clamps and at welded joints

Pipe supports must be such that they cannot damage the pipeline. That means for instance that there should be sufficient remaining support strength when one support fails. It also means that the supports should not have sharp edges. Moreover, the supports should not allow the possibility of rainwater or condensate to collect.

Pipe clamps can play an important role in causing pipe corrosion. That phenomenon can take place due to rain water or condensate entering the space between pipe and clamp. A picture of such corrosion is shown in picture 6.

Thermal insulation between a cold pipeline and its support clamp will reduce the possibility of forming a cold spot on and corrosion of the support structure. Direct contact between a stainless steel pipeline and a carbon steel support structure should be avoided to prevent corrosion of the support.

Welded joints and their heat affected zones are also more vulnerable to corrosion than the rest of the pipe. This is primarily not caused by the welding. The cause is often that the conservation of this field weld area is of a lower quality than the painting/coating of the rest of the pipe, which is executed in the shop. A picture of welded joint corrosion is shown in picture 7.

Picture 6. External corrosion under pipe clamps.

Picture 7. Corrosion at welded joints

These two forms of external corrosion can be repaired and suppressed by sand/grit blasting the pipeline at these locations to the bare metal, followed by immediately applying a coat of primer, and completed by two finish coats of paint.

6.6. Internal corrosion

Stress corrosion cracking (SCC) is a phenomenon which can occur in metals exposed to a combination of stress and corrosive environment. Liquid ammonia in the presence of oxygen can cause SCC in carbon steels. The stress levels required to initiate such cracking are high. However, the residual welding stress levels in high and medium strength materials or welds with overmatched strength, together with the applied stresses, can be enough to initiate SCC if oxygen is present in sufficient quantities.

Stress corrosion cracking has been detected in some liquid ammonia storage tanks operating at –33°C and in some ammonia pressure spheres operating at ambient temperatures. The presence of water inhibits the formation and growth of SCC [Ref 12]. In the USA it is customary to make sure that liquid ammonia contains at least 0.2% weight of water to inhibit SCC.

This phenomenon raises the question of whether SCC could also occur in carbon steel liquid ammonia pipelines. One source, apparently based on experience in the USA, states that carbon steel liquid ammonia pipelines "*have essentially no internal* *corrosion issues*" [Ref 4]. Furthermore, the EU operators of liquid ammonia pipelines confirm that SCC is not an issue in this service.

6.7. Cathodic protection

Cathodic protection is essential for the effective corrosion protection of underground and submerged pipelines. The principle of the method is to decrease the electrical potential of the object to be protected. As a result of that, the anodic reaction from iron to iron ions is suppressed to a negligible extent. The object to be protected acts as a cathode under influence of an electric "protection current".

6.8. Thermal relief

Liquid ammonia, like most liquids, expands when heated. Therefore, if a quantity of liquid ammonia is trapped in an isolated section of a line, e.g. between two tightly closed valves, it is liable to expand and pressurise the line if its temperature is raised. In practical situations this can happen typically after loading/unloading cold refrigerated liquid ammonia and the relevant pipelines are isolated when the operation is finished. It can also happen in lines associated with pumping operations where the delivery lines may be shut-off and ammonia is held between two closed valves. As the cold ammonia gets heated with the ambient heat, the thermal expansion it achieves is generally larger than the increase in volume of the line due to the thermal expansion of the pipeline material. This can cause pressure build-up and, if not relieved, can cause liquid ammonia to leak out e.g. from joints. In order to avoid this potential hazard, it is common practice to install small relief valves, which are described as thermal relief valves.

There are no industry-wide recognised criteria for provision of thermal relief valves, e.g. the threshold of liquid ammonia inventory for the installation of a thermal relief. However, guidelines developed by major EU producers show that thermal relief valves are to be provided to sections of a pipeline that can be blocked in with more than 50-100 litres of liquid ammonia. This volume criterion should not be applied without a proper consideration of the validity for a particular situation.

Thermal relief valves in this service discharge to various locations. In most cases they discharge to the atmosphere. Another option is to discharge to the next section of the pipe line. A further option is to discharge into a common vent system which may include a 'catchpot' incorporating level alarms; should one thermal relief valve discharge, an alarm is raised and the valve in question may be identified from frosting on the line.

Usually, two thermal relief valves are installed per relief location, enabling the operator to take one out of service for inspection or repair during operation.

The installation of thermal relief valves needs careful consideration as it can introduce new problems. For example, a relief valve which fails to close on a pipeline carrying liquid ammonia could lead to the total discharge of the pipe contents (between two closed isolation valves) and consequently to the chilling of the line to a potentially hazardous low temperature.

Also, when the pipeline is in operation and the thermal relief valve opens due to pressure rise in that line, it could relieve a considerable quantity of ammonia. That is notably undesirable when that ammonia is released to atmosphere (and not recovered into the next section of the pipeline or into a common vent system). For this reason a thermal relief valve on a liquid ammonia pipeline should have a large margin between set pressure and normal operating pressure.

6.9. Forces caused by pressure and temperature

All construction elements in the pipeline like valves, flanges and gaskets must be suitable for the maximum allowable operating pressure plus the external forces. All external elements must be made of carbon steel or stainless steel, with no copper containing materials (such as brass or bronze alloys) permitted.

Pipes, gaskets and all other equipment must be able to withstand pressure waves caused by changes in liquid velocity or flow direction. They must also be able to withstand forces caused by temperature differences.

6.10. Pipeline parts not in use

Valves and parts of the pipeline that are not in use, with the exception of standby lines, should be reliably isolated e.g. by blanking off using blind flanges (spectacle blinds; slip plates) or by properly designed double block and bleed valve arrangements. Dead legs should be prevented or removed.

6.11. Electrical grounding

Pipes and pipe racks must be provided with electrical grounding as a protection against electrical fault conditions, lightning and build up of static electricity, as well as to provide protection against welding currents interfering with the connected rack or piping system.

6.12. Preventing physical damage to above-ground pipelines

Pipelines (in a pipe bridge) crossing over a road should be protected by a maximum

Picture 8. Maximum height warning (A) followed by a physical barrier (B) to protect pipeline (C).

Picture 9 Example of a concrete crash barrier on a production site.

height warning, followed by a physical barrier (see picture 8). In addition to that, some companies deliberately construct these lines with extra height (for instance 5 meter).

Vulnerable sections of pipelines can be monitored by the installation of remote television cameras. These cameras may enable the operator in the control centre to take appropriate preventative action when required.

Vulnerable sections of pipelines close to roads should be protected with a physical (crash) barrier. Examples are given in pictures 9 and 10.

Pipelines in trenches near (public) roads, as well as pipelines in culverts, can be protected where necessary with a physical barrier as well. In addition to that, a protective cage construction can be provided. Such cage construction fulfils two purposes: security

Picture 10. Example of a steel crash barrier along a road side.

Picture 11. Example of a crash barrier with cage construction, protecting pipelines in a culvert.

from intruders gaining access to the line beneath the road and the safety of children who might go into the culvert which, being at a low level, can accumulate rain water and have a pool of water. This could be potentially hazardous to children. See picture 11.

6.13. Preventing physical damage to underground pipelines

Underground pipelines can suffer damage by various activities such as excavation (digging, piling etc. see Section 5.1) and physical forces (by trucks, railways and waterways). Underground pipelines can be protected from these causes by a number of measures, such as:

- Sufficient buried depth of the underground pipeline. In the EU a typical depth is 1.5 metres. It should be born in mind that sometimes the level of ground water could be so high that the pipeline may be continuously in contact with ground water and hence appropriate precautions will need to be taken.
- Line markers should be installed directly above the buried pipeline. Standing at one line marker, one should be able to see the two adjacent line markers. Line markers should also be present at locations where the pipeline changes direction. Such a line marker system will enable a proper view of the track, which will minimise the classical pipeline damage incidents by agricultural and excavation equipment. See also Section 6.3 above.
- One source [Ref 22] suggests the installation of an alarm cable, situated about half a metre above the pipeline. If that cable is hit by a digging tool, it can transmit a warning signal to the control centre of the pipeline even before the tool hits the pipeline.
- Protective guide tubes, sufficiently strong to withstand maximum forces caused by the traffic involved, should be installed around the underground pipelines where they cross roads, railways and waterways. These guide tubes will also enable smell tests to be carried out. These guide tubes are normally applicable in situations where the transported liquid ammonia is (well) above the freezing point of water to avoid freezing problems caused by water (such as rain water, condensate and ground water) leaking into the guide tube.
- Pipelines can be run through well-designed tunnels. In one EU case, a liquid ammonia pipeline passes under a 50 m wide and 14 m deep sea canal through a walkable inspection tunnel.
- In another EU case, the liquid ammonia pipeline crossing under a canal has been designed with an increased wall thickness at that particular location.

6.14. Isolation valves and remotely operated valves

Liquid ammonia pipelines should be fitted with isolation valves, preferably remotely operable. The remote system should be such that it responds in a fail safe manner in case of a power failure. The isolation valves should be located at suitable intervals to limit the loss of ammonia in the event of a pipeline failure. The distance of the intervals should be based on a consequence analysis where factors such as proximity and density of population, environmental sensitivity, pipeline characteristics (e.g. wall thickness, diameter, type of material, inspection regime), ammonia pressure and temperature, climatic and topographic conditions, and national legislation (if any) are taken into consideration. It should also be born in mind that every interruption in a solid line, e.g. by valves and flanges, is in itself a potential source of leak. Therefore, the number of such fittings should be limited. Preferably, all fittings should be welded instead of using flanges, especially in underground systems.

US practice on long liquid ammonia pipelines is to install isolation valves at such intervals that the volume that can be released between two valves is limited to 400 tonnes [Ref 1]. In the (more populated) EU areas these volumes, based on the above mentioned consequence analysis, range between about 10 and 225 tonnes.

In case of loading and unloading lines to and from ships the provision of a cable connection is recommended between ship and shore to enable the closure of emergency valves remotely from the land-based control centre as well as from the ship.

6.15. Ice formation

Operating an ammonia pipeline with ammonia at sub-zero temperatures will bring the risk of ice formation, especially if the ammonia is at -33°C or the line is uninsulated. Ice formation will cause the line to become heavier, giving an increased load on pipe supports. Furthermore, there is the possibility that the ice formation is such that equipment situated in the line, like isolation valves, can become iced in. This can be an unwanted situation because the equipment can become inoperable. If this is the case, apply appropriate vapour tight insulation, or install a heating system at the critical places. This can be electrical or steam heating.

With regard to corrosion, ice on the ammonia pipeline is not an issue. Oxygen diffusion through the ice is very slow and the low metal temperature basically reduces the corrosion rate to zero. Old ammonia pipelines that have always been covered with ice, have been known to stay in excellent condition for many years.

Most attention should be paid to corrosion when the line is intermittently operated with cold ammonia, for example a line between a sea tanker and a storage tank. During unloading of the ship, the line is cold and water condensation or ice formation occurs. When the ship is empty, the line is taken out of operation and warms up again. The formed ice melts and the wet line is then vulnerable to corrosion.

6.16. Commissioning and decommissioning

Proper precautions should be taken when commissioning and decommissioning liquid ammonia pipelines. One precaution (attention to corrosion during the warm up and cool down cycle) has already been described in the previous Section (Ice formation). Other precautions include:

A pipeline containing air should ideally be purged with nitrogen prior to introducing ammonia in order to avoid the formation of potentially explosive ammonia/air mixtures. Also, sending the ammonia/air mixture to storage facilities is undesirable because of the possibility of Stress Corrosion Cracking that can occur when oxygen is present in ammonia storage tanks.

A pipeline should be cooled down and warmed up slowly to prevent thermal stresses which can cause damage. The rate of cooling down or warming up should be in accordance with good engineering practices.

The ammonia vapour generated during the cooling process should not be disposed of by venting to atmosphere or by absorption in water followed by release to water courses. It should be returned to an ammonia recovery system.

Emptying a pipeline containing liquid ammonia should be carried out by expelling the liquid ammonia with a gas, preferably ammonia vapour. Purging the liquid ammonia line with nitrogen can result in the formation of extremely low temperatures (as low as -70°C) for which the line might not have been designed. This phenomenon is often not fully appreciated as it is generally believed that the lowest possible temperature of liquid ammonia is its atmospheric boiling point of -33°C. This is only the case when the ammonia vapour pressure above the liquid is 1 bara. When the ammonia pressure is lowered by an inert gas such as nitrogen, the boiling temperature becomes much lower. The vaporisation heat needed causes such low temperatures to occur. The liquid ammonia thus expelled should be routed to a proper location e.g. a storage tank.

An emptied pipeline which only contains ammonia vapour should be purged with nitrogen prior to allowing air to enter. As explained above, this is to avoid the formation of potentially explosive ammonia/air mixtures and to prevent Stress Corrosion Cracking when sending oxygen to storage facilities. The ammonia/nitrogen mixture leaving the pipeline should be disposed of in an environmentally acceptable way, for instance by absorbing the ammonia in water followed by recovery.

7. INSPECTION

7.1. Legislation regarding inspection

Inspection criteria for pipelines in the USA have been defined in the US Code of Federal Regulations no. 49, part 195 [Ref 13]. See Section 6.2 for some more information about that Code. Another relevant code is the American Petroleum Institute's API 570, which describes inspection, repair, alteration and rerating of in-service piping systems [Ref 23]

In the EU the EU Pressure Equipment Directive [Ref 14] is followed. However, as already mentioned in Section 6.1, this is a Directive that applies to pressurised systems in general. In most EU countries the industry has (up to now) its own specific inspection criteria for liquid ammonia pipelines. A summary of these criteria is given below.

7.2. Visual inspection

Visual inspection of liquid ammonia pipelines can help to maintain their safety and security and is, therefore, recommended. It should be carried out regularly and cover various relevant aspects which can, for example, include the following:

- condition of the surface coating, of the insulation and of the markers,
- the position (open/close) of the isolation valves, inspecting of their driving system (e.g. a check of the pressure in the associated nitrogen bottles, if any), condition of other instrumentation, condition of the stations or boxes housing the isolation valves, and of pigging units (if present),
- condition of pipe supports and of other vulnerable parts,
- condition of the safety precautions incorporated at intersections of the pipeline with roads, railroads and waterways,
- detection of small leaks via smell tests,
- detection of work (such as engineering, civil or maintenance) on adjacent pipelines to ensure integrity of the ammonia pipeline and that the correct line is used,
- detection of unauthorised excavation work or any other potentially threatening activity or situation,
- security check.

Above-ground pipelines are visually inspected at a frequency typically ranging from weekly to monthly, usually by car or other (specialised) vehicle. Special sections of the pipeline can be made continuously visible from remote television cameras. Some companies also include an annual visual inspection of the pipeline by an engineer. Exceptionally a formal visual inspection by an independent inspection authority is carried out once every few years. Visual inspection of the coating applied for corrosion

protection should be carried out on a regular basis.
Visible parts of underground pipelines, like isolation valves, associated instrumentation and pigging units, are visually inspected each day up to each month, depending on the operator. Amongst others, special attention is paid to isolation valve positions. At least one company in the EU is known to use a helicopter for its monthly visual check.

7.3. Wall thickness measurements of above-ground pipelines

Wall thickness measurements of above-ground pipelines are carried out in the EU every 1 - 10 years, with a typical average of once per 4 years. For this, simple non-destructive testing methods are available, such as ultrasonic or magnetic flux techniques. One US liquid ammonia pipeline operator reports ultrasonic wall thickness measurements per API-570 approximately every 10 years, unless a particular area is known to have corrosion under insulation, in which case these measurements are made more frequently [Ref 24].

7.4. Inspection of welded joints

The current practices for the inspection of pipeline welds during their lifetime vary in the EU operating companies. Some are of the view that non-destructive inspection of welded joints of liquid ammonia pipelines, for instance by radiography (X-ray), with magnetic particle examination or with dye penetrant examination, is not necessary. On the other hand, others do inspect welded joints. The frequency of this inspection is arbitrarily selected to be once every five years or is determined by appropriate studies or maintenance opportunities.

7.5. Inspection under pipe clamps

Pipeline parts under clamps are vulnerable to corrosion as described in Section 6.5. These pipeline parts are not visible; consequently, the condition of their surface cannot be directly visually inspected. Therefore, it is advisable to make a few clamp supports regularly accessible, selecting them randomly. This allows inspection of the pipeline surface as well as of the clamp.

7.6. Pressure test

The majority of the EU companies take the position that pressure testing after commissioning of the pipeline is sufficient; they find further pressure testing not necessary. However, some EU companies do report a policy of carrying out a pressure test. One US liquid ammonia pipeline operator reports pressure testing above-ground pipelines for barges and ships once a year, and pressure testing underground pipelines every 5 years [Ref 24].

7.7. Inspection of pipeline markings

In the case of above-ground pipelines, a check of the pipeline markings ("stickering check") should be carried out regularly. For underground pipelines (in public area), the markers should be checked ("pole check") regularly as well.

7.8. Inspection of isolation valves

Inspection of the proper operation of isolation valves should typically be carried out once per year. To that end, the valve position is blocked and then checks are made to establish if the motor is running and the shut-off time is adequate. This is also an excellent method, for gate valves that are welded to the pipeline, because gate valves have no flanges and therefore cannot be removed for inspection from the line in a non-destructive fashion.

7.9. Inspection of thermal relief valves

Thermal relief valves should be periodically removed for inspection. That can be done during operation by providing a block valve (kept locked open during operation) upstream of the thermal relief valve. For safety reasons, a proper registration system for these locked open block valves should be in place. Alternatively, in cases where two thermal relief valves are present in parallel on one pipe location, it is possible to take one out of service for inspection and repair whilst the other remains in operation. It is also possible to remove and inspect the thermal relief valves when the pipeline is out of service. Inspection frequency in the EU is 1-10 years, with a typical frequency of once per 4 years.

7.10. Insulation inspection of underground pipelines

In practice, visual inspection of the insulation on a buried liquid ammonia pipeline only takes place when there is a need to excavate the line, for instance for maintenance reasons. A useful technique to inspect the insulation of underground pipelines without the need for excavation is the DCVG (Direct Current Voltage Gradient) technique, which is described in Appendix 5. When insulation damage has been indicated, the pipe section in question should be dug out, re-insulated and reburied. Subsequently, the measurement is rechecked.

7.11. Cathodic inspection of underground pipelines

Underground pipelines are protected against corrosion by cathodic protection: see Section 6.7. Inspection of the functioning of the cathodic protection should be carried out on a regular basis. To that end a specialised contractor measures the electrical protection current and the corresponding voltage at various locations along the pipeline, as well as the "electrical pipeline potential versus ground" value. The results of these measurements show whether the underground pipeline is still a cathode and as such is protected against corrosion. Frequency of inspection is typically once per year, but some companies inspect as frequently as once every 2 weeks.

7.12. Pigging method for inspection of underground pipelines

Various companies report the use of a pigging method with their underground liquid ammonia pipeline. It is essential to clean the pipeline at various times with a traditional pig (first generation pig) before an inspection is done with an intelligent pig (second generation pig), because debris present in the pipeline can easily damage or destroy an intelligent pig. The intelligent pig can be deployed to measure wall thickness, to detect leaks, to follow movement of the pipeline (e.g. detecting deformation and/or damage), and to enable the operator to empty the pipeline in case of emergency.
The method is complex and companies had varied experiences (including failure) in its successful application.

8. LEAK DETECTION

A leak in a liquid ammonia pipeline can have considerable impact on humans, animals and nature in general: see for instance Sections 4 and 5 of this Guidance. Consequently, it is important that such leaks are detected at an early stage, enabling prompt corrective action. For that reason, various companies in the EU apply more than one leak detection system on liquid ammonia pipelines. Those systems differ considerably. Leak detection can be based on sensors, mass balance, level indication, pressure drop, acoustic signals, seismic signals and soil temperature measurement. An overview is given below.

8.1. Ammonia sensors

Escaping ammonia can be detected by ammonia sensors. Ammonia sensors are used in various locations in ammonia plants (e.g. on the compressor platform, in the synthesis area and in the refrigeration section). However, they can also be placed in loading and tank areas, and around an ammonia pipeline where they can prove a useful tool for detection of a leak from a pipeline. There are basically three commonly used types of ammonia sensors:

- *The electrochemical type*, used for sensing concentrations up to 1000 ppm. As it can accurately analyze low concentrations relevant for the protection of personnel (10-100 ppmv ammonia), it is widely used in the industry. However, the instrument has to be calibrated rather frequently (every half year) and the life time is typically limited to 3 years. The investment cost is low: some € 400 for a new sensor.
- *The solid-state type*, used for sensing concentrations up to 1-2 volume percent. This type of sensor is less accurate in the low concentration range. Calibration frequency is once per year, and its lifetime is 5-10 years. Weakness of the solid state type is its sensitivity to chemicals other than ammonia.
- *The infrared type* is also used for concentrations up to 1-2 volume percent. This type is less accurate in the low concentration range as well. Calibration frequency is once in 6-12 months. No data on lifetime are available. The big advantage of this system is that it can detect ammonia vapours over a long distance. The electrochemical and the solid state analysers are analysing a gas sample, whereas the infrared detector scans the environment for the presence of ammonia over a distance of typically 10-100 metres.

8.2. A mass balance system

This system detects spontaneous changes in the mass balance of the liquid ammonia pipeline system. Upon a leak, the mass balance system usually first gives an alarm. Specific instructions are provided for response to the alarm. When no operator action follows in a pre-determined period (e.g. 10 minutes), some systems automatically close the isolation valves in the affected part of the pipeline system or in the entire pipeline system. The consequences can be that ammonia producing plants, consuming plants and storage are likely to be affected. The mass balance system is believed not to be very accurate.

8.3. A level indication system

This system is suitable where a small capacity (typically 100 m^3) ammonia buffer vessel is present between the producing and consuming plants. Upon a leak from a connected pipeline, this system identifies a fast level drop in the liquid ammonia buffer vessel(s). When a certain criterion relating to the rate of level drop is exceeded, the system automatically (without operator interference) closes the isolation valves in the pipeline system. The consequences will be similar to those described in Section 8.2

8.4. A pressure drop system

This system reacts on deviations from normally experienced pressure drops in the liquid ammonia pipeline. It is often based on a series of pressure drop measurements. When a deviation from the predetermined setting is detected from the relevant pipeline location, the corresponding isolation valves may be automatically closed.

As this method tends to detect only big leaks, the pressure drop system is often combined with another leak detection method such as ammonia sensors or a mass balance system.

8.5. An acoustic system

This system is based on monitoring acoustic signals that travel through the pipeline in case of a leak. These signals propagate in the fluid with the speed of sound. Leaks, as small as 0.4 kg/s, can be detected. Leak detection takes place within 10 seconds, and the system calculates the location of the leak within 20 metres.

This system is a relatively new development. Only one EU liquid ammonia pipeline operator reports its installation. A description of the acoustic leak detection system can be found in Appendix 3.

8.6. A seismic system

Another technology that is able to detect leaks in pipeline systems is based on a seismic principle. The system consists of seismic sensors, which are deployed along the pipeline and in its vicinity. These wireless sensors pick up any activity which creates a seismic signal in the ground. Subsequently, the sensor or sensors relay the picked up signal to a processing unit, which analyses the data to determine the nature of the event that generated that seismic signal. The system can distinguish between different events such as a person walking, vehicle driving, heavy machinery activity (such as excavations), digging, hitting, drilling into the pipeline, leaks etc.

The processed data is transmitted to the control centre of the pipeline operator. Real-time warning is displayed to the operator, which includes the location and classification of the event. These two parameters (location and classification) enable the operator to take appropriate action.

The system is applicable to both above-ground and underground pipelines. It is reported to have been installed on various water and oil pipelines in Asia and Latin America. So far, there is no application reported on liquid ammonia pipelines [Ref 16].

8.7. A soil temperature system

One source [Ref 22] suggests the installation of an optical fibre system that identifies a change in soil temperature upon a leak in a buried pipeline. These fibre systems should be positioned alongside and above the pipeline, and be coupled to an appropriate interpretation system. There is also expensive technology available than can even specify the estimated location of the leak.

The system is notably applicable to underground pipelines, although application to above-ground pipelines should not be ruled out at this stage. However, no report of actual installation could be identified, and the system should therefore be characterised as an emerging technique.

9. MITIGATION AND EMERGENCY RESPONSE

9.1. Behaviour of ammonia on loss of containment

Ammonia gas or vapour, at ambient temperature as well as at -33°C (normal boiling point) is lighter than the ambient air; consequently, any release of the vapour alone forms a buoyant plume, dispersing upwards in the atmosphere [Ref 9].

When liquid ammonia is suddenly released from a pressurised liquid line, part of the ammonia is vaporised. The escaping plume tends to be made up of flashed off ammonia vapour, entrained droplets of liquid ammonia and entrained ambient air. The degree of vapour flash is dependent on the temperature and pressure of liquid ammonia. Pools of cold (–33°C) liquid ammonia on the ground can be formed either as a result of rainout from the release or from spills from the line.

After an initial flash caused by the decrease in pressure and input of conductive heat from the ground, the pool gradually cools down by convective vaporisation and adiabatic saturation of air. The resulting cold mixture of air and ammonia will be heavier than the ambient air in most cases. The chilling effect produced either due to flashing or adiabatic saturation can cause visibility difficulties within the plume, particularly near the source of release a white dense fog will be formed.

As soon as an ammonia release has been detected, measures must be taken to stop the release, if safe to do so, and to get the consequences under control.

9.2. Protection of the surrounding communities

Immediate warnings must be issued when an ammonia incident has taken place whereby the escaping ammonia can affect the population.

When an ammonia escape is potentially threatening, the population living downwind of the incident may have to evacuate. However evacuation takes time and that is why evacuation is often potentially unsafe or impossible.

The population living in the danger zone needs to be warned as soon as possible. They need to be advised to stay inside, close all doors, windows and ventilation openings and to use wet towels to cover openings under doors and windows. In the event of a prolonged release it may, however, become necessary to carry out evacuation.

9.3. Limiting the release

Attempts should be made to reduce the rate of escape of ammonia.

When liquid ammonia escapes from a line, the pressure in the line is likely to stay constant as long as the source has liquid ammonia inventory.

Since the water that is normally available to control ammonia gas clouds is warmer than the pipeline containing the cold boiling ammonia, the leaking pipeline should not be sprayed with water.

The release can be controlled by:

- Isolating the leaking part of the line
- In case of a leaking valve or flange: repair.

9.4. Limiting the vaporisation

Vaporisation of the released ammonia can be controlled by:

- Limiting the size of the liquid ammonia pool.
  Construction of an earth dike or the use of sandbags can be very effective for limiting the pool size. This will limit the heat input from the ground.
- Covering the liquid ammonia pool with a layer of fire-fighting foam.
  The foam layer will limit the heat input from the air.
- Breaking the jet of a spray release.
  If an obstacle e.g. a screen is placed in the path of a spray or jet, some of the liquid droplets present in it can separate out forming a pool on the ground.

9.5. Dissolving ammonia in water.

Ammonia dissolves very well in water. To be effective, large quantities of water are needed.

Never spray water directly into a pool of liquid ammonia unless a hundredfold excess of water is immediately available.

9.6. Lowering the concentration of ammonia gas/vapour in air

When a cold ammonia cloud mixes with air a white fog in the form of an aerosol is formed, which is heavier than air. The gas cloud travels close to the ground.

The gas cloud and the aerosol can be fought effectively with water screens or water curtains set up in the path of a travelling plume. The water screens should be placed between the release point and the threatened area. Multiple water screens may be necessary to get a good coverage of the plume by the water curtains and to supply as much water as possible.

9.7. Fire fighting measures

Ammonia vapour, discharges from lines and liquid spills are difficult to ignite, particularly in the open air. In an enclosed space, mixtures of ammonia and air within the limits (16 - 27 vol% ammonia in air) might cause explosion when ignited.

Actions recommended in the event of an indoor release.

- Attempt to isolate source of leak
- Use foam, dry powder or CO_2
- Use water sprays to cool fire-exposed lines, containers and structures; to disperse vapours and to protect personnel.
- Do not spray water into liquid ammonia.
- Wear self-contained breathing apparatus and full protective clothing.

A cold, dense cloud of ammonia may impair visibility.

9.8. Emergency measures.

The following is a summary of the emergency response measures:

- Approach the place of the accident from upwind.
- Wear full protective clothing including respiratory protection.
- Warn people immediately if the escaping ammonia can affect them.
- Evacuate the area down-wind of the release only if it is safe to do so and the release is life-threatening.
- Isolate the source of the leak as quickly as possible using trained personnel, if safe to do so.
- Contain the spillage if possible.
- Remove ignition sources.
- Consider covering the liquid pool with foam to reduce evaporation.
- Use water sprays to combat gas clouds. Do not apply water directly into large ammonia spills.
- In case of fire use water sprays to cool fire-exposed containers.
- Take care to avoid the contamination of watercourses.
- Inform the appropriate authorities in case of accidental contamination of watercourses or drains.

9.9. Emergency plans

Emergency plans should be prepared to cover incidents involving release of ammonia from pipelines as well as from other site inventories. In some countries there are regulations relating to inter site pipelines which may specify provision of emergency plans.

Sites where large quantities of (> 50 tonnes) ammonia are present are subject to the Seveso Directive [Ref 17]. Article 9 of this directive requires the operator to prepare on-site and off-site emergency plans and to produce a safety report.

Appropriate exercises (test drills) should be carried out to test the emergency plans at suitable intervals, in conjunction with the relevant services and authorities, using ammonia release scenarios applicable to the installation. The plans should be reviewed and improved based on the lessons learnt from such exercises.

10. GLOSSARY & EXPLANATION OF TERMS

API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
CAS	Chemical Abstracts Service
DIN	Deutsches Institut für Normung
DCVG	Direct Current Voltage Gradient
EGIG	European Gas pipeline Incident data Group
EINECS	European INventory of Existing Commercial Substances
GHS	Globally Harmonised System
IOELV	Indicative Occupational Exposure Limit Value
LC50	Lethal Concentration (median) for 50% of the population under test
MAC	Maximum Allowable Concentration
PN	Polska Norma
SCC	Stress Corrosion Cracking
STEL	Short Term Exposure Limit
TGL	Technische Güte und Lieferbedingungen
TWA	Time Weighted Average

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APPENDICES

1. Design codes and national rules for the design of liquid ammonia pipelines in various EU Member States
2. Materials of construction applied in liquid ammonia pipelines in various EU Member States.
3. Description of an acoustic ammonia leak detection system.
4. Nomogram showing properties of ammonia.
5. Technique for insulation surveys on underground pipelines.

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APPENDIX 1

Design codes and national rules for the design of liquid ammonia pipelines in various EU Member States

Belgium	Pipeline 1 and 2	DIN, Koninklijk, Besluit 11 March 1966
Germany	Pipeline 1 and 2 Pipeline 3	pN 40 TGL 190-354 01/03/04/16
Italy	Pipeline 1	SNAM specifications, ASME B31.3/4/8
Netherlands	Pipeline 1 Pipeline 2	DIN, ASME (not further specified) ASME B31.3
Poland	Pipeline 1 Pipeline 2, 3, 4 and 5	Unknown PN
Portugal	Pipeline 1	ANSI B31.3
Spain	Pipeline 1 Pipeline2 Pipeline 3 and 4	ANSI B31.3 ASME B31.3 ASA B31.1
U.K.	Pipeline 1, 2, 3, 4 and 5 Pipeline 6 and 7	B31.3 B31.3

Note 1: The pipeline numbers refer to those in Table 1.
Note 2: ASA B31.1 is equivalent to ASME B31.1.
Note 3: B31.3 and ANSI B31.3 are equivalent to ASME B31.3

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APPENDIX 2

Materials of construction applied in liquid ammonia pipelines in various EU Member States

Belgium	Pipeline 1 and 2	Carbon steel TTSt35 (very fine grain), and stainless steel 1.4541
Germany	Pipeline 1 and 2 Pipeline 3	Carbon steel (not further specified) Carbon steel, H52-3 (similar to TSTE 355 or ASTM A 537)
Italy	Pipeline 1	API 5L GrB, fully killed, Charpy V tested at -45°C
Netherlands	Pipeline 1 Pipeline 2	Carbon steel ASTM333 Gr6, and stainless steel ASTM312 TP304L ASTM A312 TP 304L (is Symbol AISI 304L, is Number 1.4306)
Poland	Pipeline 1 Pipeline 2, 3, 4 and 5	Carbon steel (no type specified) Carbon steel type 18G2A and API 5L GrB seamless
Portugal	Pipeline 1	A 333 Gr.6 / TT st.35 / A333 Gr.1
Spain	Pipeline 1 Pipeline2 Pipeline 3 and 4	A 333 Gr.6 ASTM A 333 Gr.6 ASTM A 333 Gr.6 and St-35
U.K.	Pipeline 1, 2, 3, 4 and 5 Pipeline 6 and 7	LT50 (a type of CS) and sometimes also SS (type not specified) Carbon steel (12'' line) and stainless steel (3'' line) ; not further specified

Note: The pipeline numbers refer to those in Table 1 on page 7.

Material names conversion table:

Steel	EU Norm	Symbol *	Number **
TT St 35 N/V	10216-4	P255 QL	1.0452
TTSTE355	10216-3	P355 NL1	1.0566
1.4541	10028-7	X10CrNiTi 1810	1.4541
A 333 Gr6	10208-2	L245 MB	1.0418
API 5L GrB	10216-2	P 235 GH	1.0345

**) This symbol provides a designation for the material. It is in many cases a trade symbol defined by the supplier.*
***) "Werkstoffnummer" (material number) as used in the German Stahlschlüssel.*

APPENDIX 3

Description of an acoustic ammonia leak detection system

Basic principle of the acoustic leak detection system

The acoustic leak detection system detects small leaks quickly and provides a means of limiting total product loss. Wall failure of a pipeline under pressure is a sudden event which occurs when the internal pressure produces a sudden rupture in a pipe wall. When the hole forms, fluid escapes in the form of a high velocity jet. The fluid loss produces a sudden pressure drop which propagates in both directions from the hole as acoustic signals within the pipeline with the following characteristics:

1. The pressure loss travels over large distances within the pipeline due to low signal absorption loss and because the pipe walls guide the wave fronts.
2. Signals propagate in the fluid at the speed of sound.
3. Pressure loss is detectable as an acoustic signal.
4. The amplitude of the acoustic signal increases with leak size.

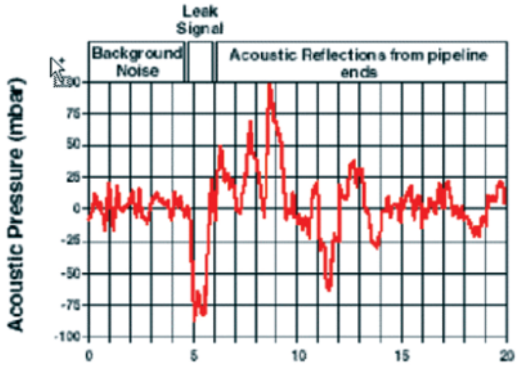
The WaveAlert® Acoustic Leak Detection System makes use of these characteristics to provide the following information:

- That a leak has occurred
- Where the leak is located

Dynamic pressure transducers with transient response characteristics (typical ≤ 1msec) permitting detection of rapid pressure variations are used at valve locations and at the pipeline ends. An analog pressure output is provided by a 4-20 mA signal from a preamplifier/transmitter located within the transducer housing.

Analog acoustic pressure signals are monitored directly by the locally installed site processors. A dedicated high speed processor samples acoustic signals at fixed intervals, repeatedly comparing the acoustic pressure profile with a mask representing a characteristic leak shape. Digital band pass, moving average filters and other filters are also used to discriminate against non-leak noise. The system can also be used to automatically shut the pipeline in the event of a detected leak.

A schematic overview of the system and the principles of acoustic signals is given below.

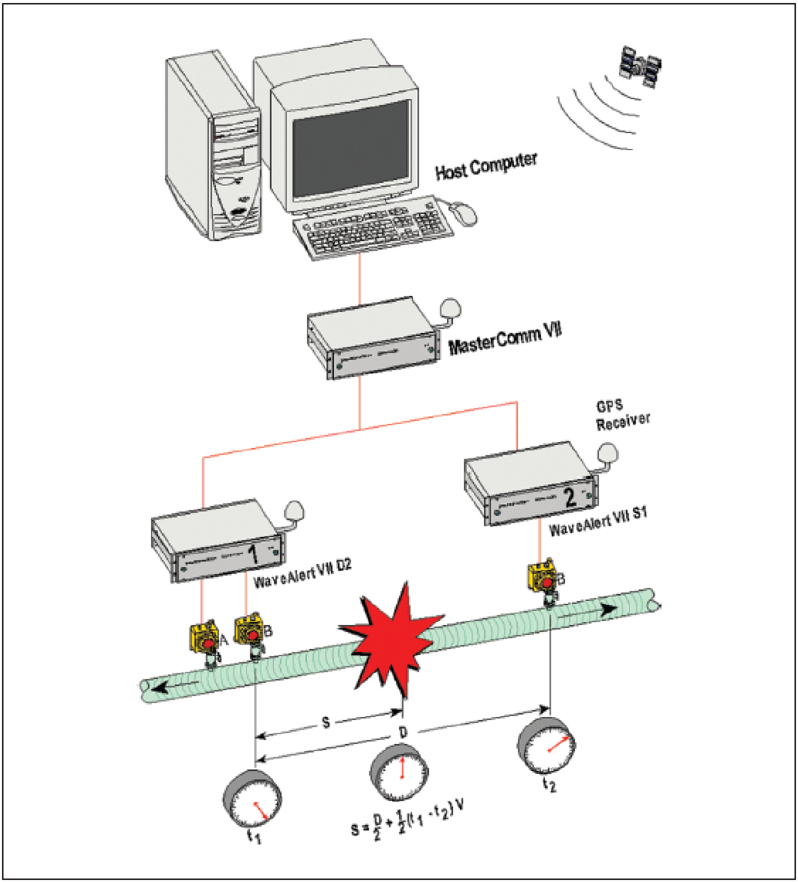


Distance between sensors

Attenuation of the acoustic pressure signal when it travels from leak point to the sensors and the leak size itself determine if comparison against the pressure profile mask will result in a successful leak declaration when a leak occurs. So, in theory, to determine what maximum distance can be applied depends on the leak size the system needs to detect and the allowable time interval to detect this leak. A more realistic approach however is to look at the pipe system and its potential leak positions to design the system in the most cost effective way. The maximum distance between a pressure sensor and a site processor is limited to 500 m. In the most basic configuration a maximum distance of 1 km can be covered.

Advantages/disadvantages

- Detects small leaks
- Leaks are detected in a very short time
- Leak location is determined
- The system is equipped with 'electronic' test facilities to simulate a leak
- The system can be equipped with a real leak test system
- Reliable, easy to use and maintain
- Independent of flow rate and operating conditions (pump start-up/shut down, valve open/close)

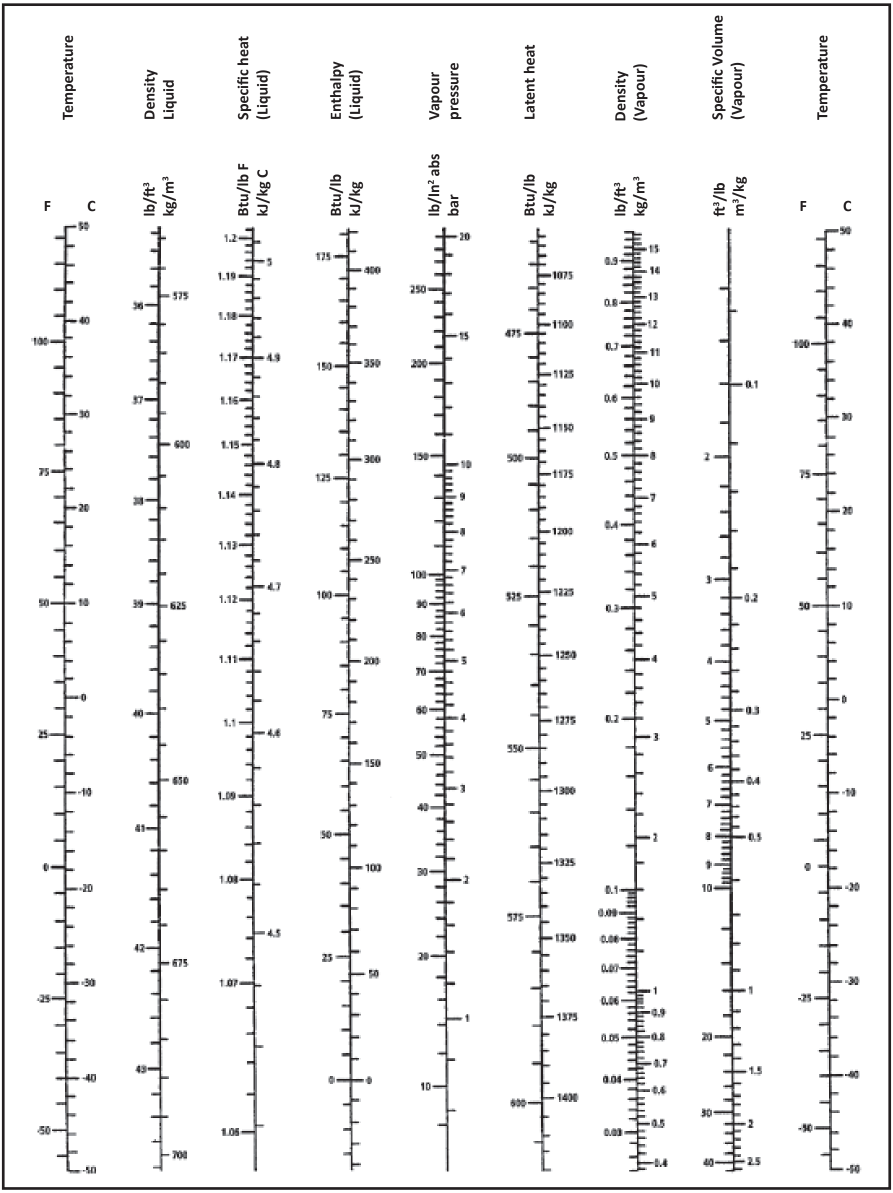


An example of a typical application in an EU liquid ammonia pipeline

1. Detectable leak from 0.4 kg/s (4 mm hole)
2. Leak detection within 10 seconds
3. Leak location within 20 m
4. System tested with real leaks. Score 100%.

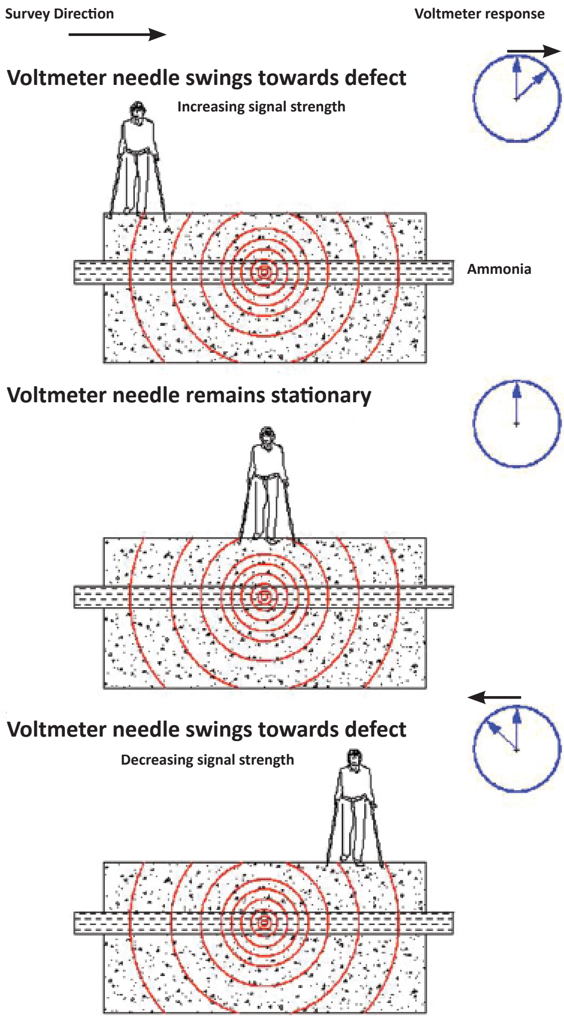
APPENDIX 4

Nomogram showing properties of ammonia [Ref 21]



APPENDIX 5

Technique for insulation surveys on underground pipelines



The **DCVG** (Direct Current Voltage Gradient) is a technique for insulation surveys on underground pipelines.

When a DC is applied (in the same manner as in cathodic protection) to a pipeline, a voltage gradient is established in the ground due to the passage of current through the resistive soil to the bare steel exposed at an insulation fault.

The technique is fundamentally based on measuring the voltage gradients in the soil above a cathodically protected pipeline.

In the DCVG methodology, the DC input signal used to measure the voltage gradient is pulsed trough the cathodic protection at 1.1 Hz (0.3 s ON 0.6 s OFF). The method requires the gradient measurements to be made with a sensitive milli-voltmeter and two copper-copper sulphate electrodes placed about one metre apart from the operator. In a voltage gradient one electrode will adopt a more positive potential than the other which enables the size and position if the gradient to be established.

For the insulation survey, the surveyor walks the pipeline route testing at regular intervals with the electrodes, parallel, preferably above the pipeline and separated by one to two metres. As a coating fault is approached, the surveyor will see the milli-volt meter start to respond to the ON/OFF pulsed current. When the fault is passed, the needle deflection reverses and decreases as the surveyor walks away from the fault. By retracing, the position of the probes can be found where the needle shows no deflection. The fault gradient epicentre is then sited midway between the two copper/copper sulphate electrodes.

There are some limitations for this method, and the measurements must always be evaluated and some parameters taken into account in order to understand them. Soil resistivity, temperature, pH and stray currents can influence the validity of the survey results.

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Product Stewardship is defined as "the management of the safety, health and environmental aspects of a product throughout its lifecycle in an ethically responsible way". It is Responsible Care as applied to products. In our application of Product Stewardship we cover the total value chain, but also address additional issues such as Best Practices that are not necessarily just dealing with the product characteristics.

For the fertilizer industry, Product Stewardship is ensuring that fertilizers and their raw materials, additives and intermediate products are processed and manufactured, handled, stored, distributed and used in a safe way with regard to health, occupational and public safety, environment, and security. This includes supplying plant nutrients which satisfy society's requirements for the safe production of food and animal feed.
The Product Stewardship Program of Fertilizers Europe provides:

- a guidance on how to establish a Product Stewardship Program on a Company level
- agreeing with Fertilizers Europe standards on the production, distribution, storage and use of fertilizers
- reference to EU legislation, industry practices and best available techniques

The scope is limited to EU legislation and does not cover any specific National Requirements.

The Product Stewardship Program covers mineral fertilizers, their raw materials and intermediate products.

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