GUIDANCE FOR THE STORAGE OF HOT AMMONIUM NITRATE SOLUTIONS

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efma european fertilizer manufacturers association

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CONTENTS

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1. INTRODUCTION

This guidance is one of several published by EFMA in order to promote safety in the fertilizer industry. It replaces the previous one, which was issued by the industry associations IFA/APEA in 1985 (Ref. 1). It is much more detailed and takes into account the findings of the recent research work carried by TNO, a research organisation located in the Netherlands.

TNO, at the request of EFMA, investigated the safety aspects of ammonium nitrate solutions at high temperatures and reported in 2003 (Ref. 2). The EFMA steering group overseeing this work saw the opportunity as well as the necessity to follow up this project with the preparation of a more detailed guidance for the safe storage of hot ammonium nitrate solutions. This guidance seeks to translate the pertinent results of the EFMA/TNO investigation into practical recommendations and also to encompass the results of intensive discussions within the steering group.

2. SCOPE AND PRINCIPLES

This guidance concerns the storage of hot ammonium nitrate solutions with a concentration in excess of 80% in fixed tanks. The recommendations are not intended for tanks used as process vessels in manufacturing plants. This guidance may also serve to determine the basic safety concept in performing safety studies and the design of storage tanks related to hot ammonium nitrate solutions.

This guidance is intended to apply to new installations but consideration must be given to adapting existing installations wherever reasonably practicable. It must also be borne in mind that not all recommendations may apply in every situation and retrofitting or modifying existing installations may not always be possible from a technical or practical point of view. In such cases appropriate safety studies should be carried out to establish that the existing situation is acceptable.

The guidance is not prescriptive in nature but provides a series of recommendations. It attempts to describe the relevant factors, their relative importance and various options available to specific situations.

This guidance addresses various safety related aspects of the storage of ammonium nitrate solutions, for example, location, design, construction, instrumentation, control systems and relief devices. It also briefly considers environmental aspects. In relation to safety it mainly covers:

- Location and construction features
- Design features concerning, for example, heating coils and venting methods
- Safety equipment and first aid measures
- Normal process conditions (e.g. temperature, pH)
- Upset conditions (monitoring and prevention)
- Decomposition reactions (e.g. detection by changes in temperature, pH and concentrations of N_2O, NO_x etc.)
- Intervention techniques such as the addition of water and/or ammonia and dumping of the tank contents into a safe area.

Local site conditions need to be taken into account in considering all the aspects described in this guidance.

The guidance briefly describes the physical and chemical properties of AN, focusing on the potential hazards of hot AN solutions. It also covers the main regulations, which apply to the production and storage of hot ammonium nitrate solutions in the European Union. Readers are advised to refer to up-to-date regulations as there may have been changes since the publication of this guidance.

3. PROPERTIES OF HOT CONCENTRATED SOLUTIONS OF AMMONIUM NITRATE

The main properties of relevance for AN storage are summarised below; further information is given in the Safety Data Sheet in Appendix 1. Much information on the physical and chemical properties and potential hazards of ammonium nitrate is available in literature (Ref. 3-6).

3.1. Physical Properties

Ammonium nitrate is very soluble in water. Heat is absorbed when it dissolves, which makes the process of dissolution difficult and slow at low temperatures.

The crystallisation temperatures as well as the atmospheric boiling points of AN solutions of different concentrations are given in the table on next page.

Crystallisation Temperatures and Boiling Points of AN Solutions

AMMONIUM NITRATE (%)	80	82.5	85	87.5	90	92.5	95	98
Crystallisation temperature (°C)	57	65	75	85	96	108	122	146
Atmospheric boiling point (°C)	128	132	136	140	146	155	168	203

More detailed information regarding the relationship of atmospheric pressure boiling and crystallisation temperatures of AN solution is given in Diagram 1.

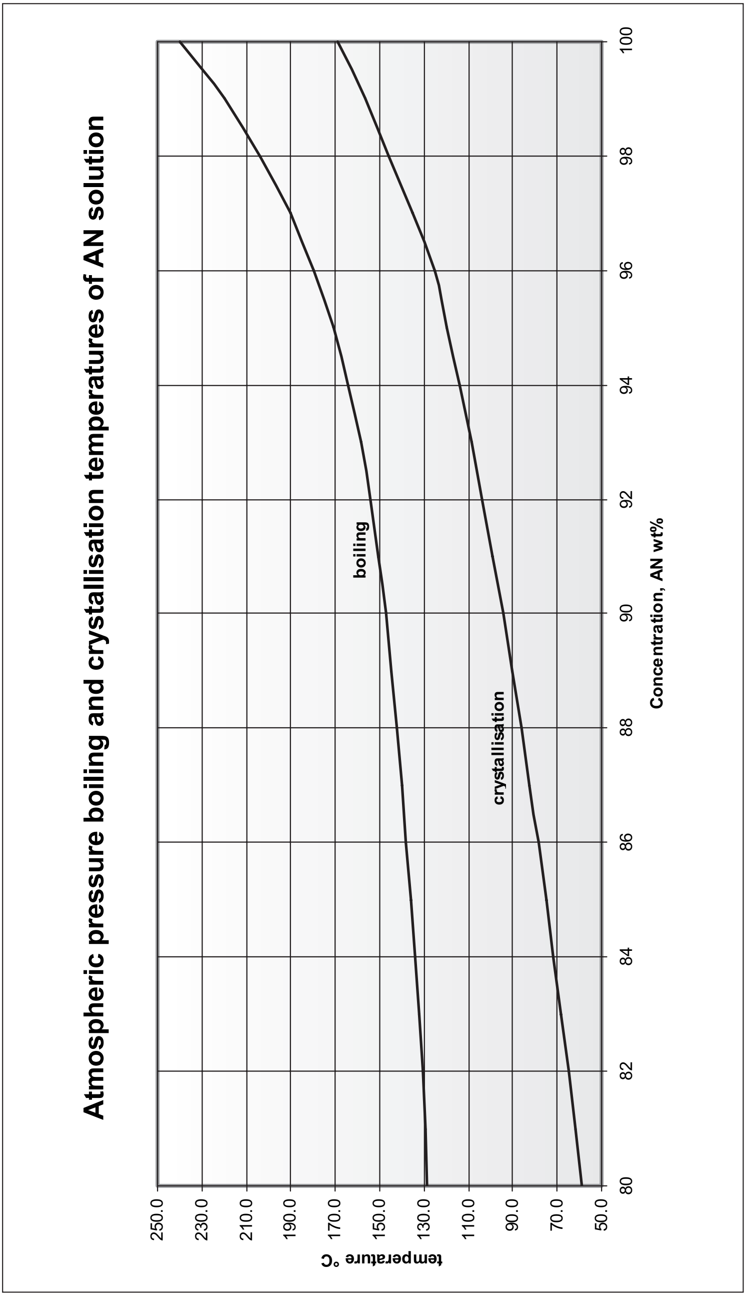
3.2. Chemical Properties

Hot AN solutions should always be stored under neutral or alkaline conditions. It is common industrial practice to express the pH of an AN solution as that of a 10 wt% solution at 25°C. According to this practice the pH of a neutral AN solution is not 7 but is in the region of 4.5. Measuring the pH at different concentrations and/or temperatures will result in different values and these values need to be appropriately adjusted.

AN solutions themselves are neither combustible nor flammable. They are oxidizing in nature and thus can enhance the potential fire hazard of combustible material. They can react on contact with organic materials such as wood, oil or grease, in some situations after a delay.

Hot AN solutions are capable of thermal decomposition which is negligible under normal storage conditions. Decomposing ammonium nitrate solutions can evolve N_2O, brown nitrous fumes (NO_x), nitric acid vapours and NH_3, some of which are toxic in nature and, therefore, should not be inhaled (see Section 8 below). Whereas most of the decomposition reactions are exothermic in nature, the dissociation reaction (into ammonia and nitric acid) is endothermic and is vapour-pressure-dependent.

The tendency to decompose is enhanced by high temperature, acidic conditions and the presence of contaminants containing ions of,



Atmospheric pressure boiling and crystallisation temperatures of AN solution
temperature °C
250.0
230.0
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
80
82
84
86
88
90
92
94
96
98
100
Concentration, AN wt%
boiling
crystallisation

Diagram 1

e.g. Cl, Fe, Co, Ni, Cr, and Cu. AN solutions also react vigorously with zinc and zinc alloys (note that zinc is widely used in galvanised steel). Once started, these reactions can become progressively more severe, unless controlled (see Section 5.3 below).

In this guidance the two types of reactions, decomposition/ dissociation and oxidation, are described simply as decomposition.

Hot concentrated AN solution can give rise to a potential explosion hazard when heated under confinement (e.g. in a blocked pipe) or by severe shock derived from a high explosive or a high velocity projectile.

3.3. Environmental Aspects

Ammonium nitrate has a low toxicity to aquatic life (see Safety Data Sheet in appendix 1). It is the free or non-ionised ammonia generated due to the dissociation (which tends to be small) of AN, which produces the toxic effects. Ammonium Nitrate is a nitrogen fertilizer. Heavy spillage may cause an adverse environmental impact such as eutrophication in confined surface waters, or nitrate contamination. AN is biodegradable and does not show any bioaccumulation phenomena.

3.4. Health Hazards

In respect of people, AN is generally considered to be of low toxicity through all major absorption routes. Hot concentrated solutions of AN can produce very severe burns on the skin. This is not only because of their high temperature but also because they attack the skin on account of their oxidizing properties (see Safety Data Sheet in Appendix 1). First aid details are given in Section 8 below.

A toxic hazard can arise from brown nitrous fumes given off by decomposing ammonium nitrate solutions. These fumes must not be inhaled and they can have an insidious and delayed effect (see Appendix 1).

Protective measures should be taken in case ammonia is present in the area near the storage tank, for example, due to over-ammoniation and local venting.

4. LOCATION, DESIGN AND INSTRUMENTATION

4.1. General

Safety studies shall be performed for all new installations. They should be reviewed on a regular basis (e.g. every few years).

During the safety study attention should be paid to other processes linked to the manufacture and storage of AN solution with special consideration to the risk of contamination.

4.2. Location

A tank for hot concentrated ammonium nitrate solution should not be located close to any storage of combustible materials, whether solid or liquid.

The location for an AN solution storage tank should be selected so as to minimise the risk of contamination by acids and by other non-compatible materials as indicated above in Section 3.2.

If road tankers or rail wagons are required to park near a tank, the parking area should be level and arranged in such a way that, in case of a leak, the hot solution does not run into a common drain where it might react violently with other materials. A sump should be provided at filling points so that any drips can be dealt with in a controlled manner. Wooden sleepers should not be used for railway lines in the loading area.

Care should be taken to prevent any vehicle colliding with a tank, its supports, or its pipeline supports, by the erection of barriers where necessary.

4.3. Tank Design

The tank should be constructed to an appropriate engineering standard and the material of construction, such as austenitic stainless steel 304L, shall be resistant to corrosion by hot concentrated ammonium nitrate.

The following behaviour of ammonium nitrate should be borne in mind when considering the design of a new tank with respect to diameter and height aspects. Tanks with a low height have the advantage of giving rise to a lower pressure head above the ammonium nitrate solution at the bottom of the tank. This reduces the boiling temperature and the associated decomposition rate at the bottom of the tank. On the other hand, a low height-to-diameter ratio could be disadvantageous from the point of view of the mixing of any added dilution water.

Care should be taken to avoid confined or semi-confined spaces within the tank and associated equipment which can potentially allow AN solution to be trapped. For example, avoid double skinned baffles inside the tank.

Thermal insulation, if applied, should be of inorganic material and should be checked to ensure there is no hazardous reaction of the material with hot ammonium nitrate solution.

The insulation should be protected and sealed by an outer skin of stainless steel or aluminium. Whichever is used, care should be taken to ensure that there are no gaps in the outer skin to prevent water entering which could reduce the efficiency of the insulation.

The number of flanges should be kept to a minimum and they should be outside the insulation of the tank.

There should be a facility such as a pump to circulate the solution in the tank to ensure a homogeneous solution. A minimum circulation rate should be considered for each individual tank and, in the absence of suitable calculation methods to specify this rate, a minimum circulation rate of about 5-10% of the tank volume per hour is recommended as a rough guide.

The tank should be provided with a secondary containment (e.g. bund wall). The area contained within the secondary containment must be free from reactive substances and from surface contamination to minimise the risk of AN decomposition and associated toxic fume release if the solution leaks or there is a major loss of containment.

The tank should be provided with an overflow system with the discharge directed to a safe area. Care should be taken to avoid this line blocking due to crystallisation of the AN.

The materials used for the foundation underneath a tank should be devoid of a sensitising effect on ammonium nitrate to minimise the risk of decomposition in case of a leak of the ammonium nitrate solution.

The design should pay attention to the detection of leaks occurring due to corrosion, for example.

The interior of the tank shall be thoroughly cleaned after construction and before any internal repairs. The tanks shall be inspected and cleaned if necessary on completion of the repairs.

It should be noted that ammonium nitrate solutions, whether hot, cold, concentrated or dilute, can attack and cause damage to cement and concrete unless they are suitably protected.

Refer to Section 4.4 for the provision of instruments, controls and various accessories which should be considered when designing the tank.

The tank should be provided with a reliable water addition facility to cool and dilute the tank contents in case of a temperature rise e.g. caused by a decomposition of the AN solution in the tank.

4.4. Instruments, Controls and Accessories

Design standards concerning safety integrity

International guidelines have been developed for Safety Integrity Levels (SIL). The International Electrotechnical Commission (IEC) has issued:

- IEC 61508-SER "Functional safety of electrical/electronic/programmable electronic safety-related systems" and
- IEC 61511-SER "Functional safety: Safety Instrumented Systems for the process industry sector".

At the time of printing of this guidance the codes are not mandatory but it is expected that EU and national guidelines will be based on these. Readers are advised to consult these codes when designing AN solution storage systems.

Safety reviews of the individual plants can be used to determine the required SILs of safety instrumented functions (SIF) such as the water addition system activated by high temperature. It is outside the scope of this guidance to give detailed recommendations in this regard.

Level

The tank must be provided with reliable level measuring instruments capable of giving a continuous indication of level and high/low level alarms. In selecting the level instruments care must be taken for varying concentrations, densities and crystallisation temperatures of ammonium nitrate solutions.

Temperature

Multiple temperature sensors should be provided, preferably at different heights and around the circumference of the storage vessel. High temperature alarms/trips should be installed with set points at temperatures as close as practically possible to the operating temperature. The indicative range for such settings is 5-20°C above the normal operating temperature. The minimum operating temperature should be at least 5°C above the AN solution crystallisation temperature. A low temperature alarm should also be provided to warn of the risk of crystallisation.

Sampling

A means (e.g. a sampling valve) for obtaining a representative sample of the solution should be provided. Where necessary, a steam injection point for keeping the sampling lines clear should be installed.

Venting

A vent should be provided on the tank to prevent it from being put under excessive pressure or vacuum. Care should be taken to keep the vent free from blocking by proper design or by steam tracing or jacketing, where this is considered necessary.

The results of the EFMA study relating to the release of decomposition gases including water vapour (also generated by water addition) should be taken into account. In order to provide a sufficient safety margin for the vent sizing, its capacity should be calculated corresponding to the credible worst-case scenario for the particular installation.

For example, a selected scenario involving a solution (100 tes) with a pH of 2 and chloride contamination of 100ppm leads to a vent size in the region of 250-300mm diameter. This takes account of the gases formed by decomposition as well as the gases from the evaporation of water, added at a rate sufficient to bring the temperature down from 180 to 150°C in one hour. The vent size is dependent on the rate of water addition.

Valves

Valves which do not trap the solution within the internals, are recommended for ammonium nitrate solution duty.

An automatic valve or a manual valve operable from a safe distance, may be considered for emptying the storage tank (see Section 5.3) as an alternative to water addition where water cannot be relied upon to be available. A drain valve should be provided to enable the tank to be emptied completely, where practicable.

Steam coil

A steam heating coil, or a circulation system incorporating a heat exchanger, may be provided to safeguard against low temperature conditions. The steam supplied shall be saturated and controlled so that the temperature of the ammonium nitrate solution does not exceed 150°C.

The following precautions are recommended for the steam supply system:

- The steam pressure in the coil should always be such that in case of a leak occurring in the coil the solution would not flow into the coil.
- The steam in the coil should preferably be on pressure control, not on temperature control in order to satisfy the above condition.
- The steam supply system should be fitted with protections to avoid the use of superheated or over-pressure steam.

Other control measures

Facilities for adding gaseous ammonia can be provided to correct the pH of the solution. This can be done either by direct injection or by circulation through another vessel which is equipped with the facilities for ammonia addition.

Pumps

Pumps are required to circulate the ammonium nitrate solution, to transfer the solution and to empty the storage tank.

They should be adequately protected to avoid pumping against a dead-end and overheating. Written procedures should be available for the design, operation and maintenance of these pumps. The pump system should be designed so as to minimise the risk of cavitation e.g. by means of a low level switch in the tank.

Pipework

The hardware and control systems linking the storage with the plant and exporting facilities (e.g. tanker loading) should be designed in such a way as to minimise the risk of contaminating the stored solution.

Unwanted pipe connections to the storage tank should be avoided in order to minimise the risk of contamination.

Pipe work should be steam jacketed or steam traced and/or insulated, as appropriate. It should be run with an adequate slope for drainage with drain valves at the lowest points. See above under steam coil for precautions relating to the steam supply.

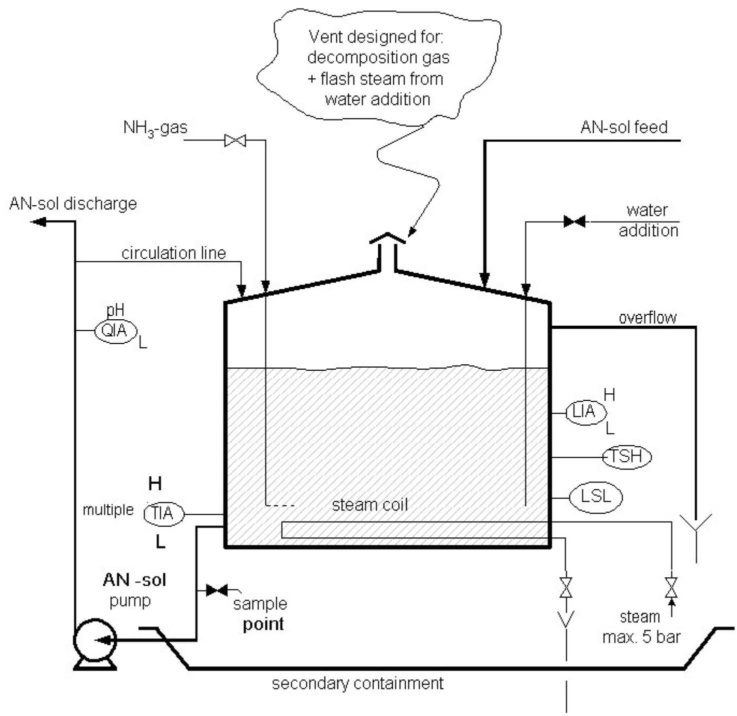
AN solution lines can also be heated by electrical tracing as an alternative to jacketing or steam tracing. Heating by electrical tracing is generally not recommended as a permanent provision but if used, sufficient precautions should be taken. The tape should be the inherently safe, temperature-'self-limiting' type to avoid potential 'hot-spots'. The maximum achievable temperature should not exceed the safe design temperature in the line; just as such a limit would be applied in the case of steam tracing. Independent measurements such as the temperature of the tracing tape and the electric current at the beginning and end of the tape should be used to ensure proper operation of the electrical tracing.

Care should be taken in design and modifications to prevent trapping ammonium nitrate in isolated sections. Steam/Condensate injection points should be provided to flush or clear the lines where appropriate.

Proper sealing should be provided, e.g. by using spiral-wound gaskets, to prevent the leakage of AN solution from flanges.

4.5. Typical Storage Tank Layout

Figure 1 is an illustrative drawing of a storage tank with its safety provisions. Different configurations and different degrees of automation can be envisaged depending on the local situation.



QIA	Quality Indicating Alarm (in this case: on-line pH measurement)
TIA	Temperature Indicating Alarm
LIA	Level Indicating Alarm
TSH	Temperature Switch High
LSL	Level Switch Low

Figure 1 – Illustrative drawing of a typical AN solution storage tank

5. OPERATION

5.1. General

The operation of the installation should be in accordance with written instructions. They should be available on the site, should cover the necessary safety precautions and include good house-keeping rules.

5.2. Normal Operation

Temperature monitoring and control

A maximum temperature of 150°C was recommended for the stored solution in the previous Guidance (Ref. 1). The results of the recent EFMA project (Ref. 2) tend to support this limit.

The operating temperature of the AN solution shall be monitored and controlled to keep it below 150°C.

The minimum operating temperature should be at least 5°C above the AN solution crystallisation temperature.

pH monitoring and control

The pH of ammonium nitrate solutions should be regularly monitored and kept at neutral or alkaline i.e pH >4.5 (see Section 3.2).

AN solutions tend to lose ammonia gradually during storage. The more alkaline the solution the higher is the loss of ammonia.

Regular manual sampling and analyses or in-line continuous pH measurement shall be performed according to written procedures. The sample should be representative of the total content of the tank, e.g. by taking the sample from the circulation line. Such a sample should be taken and analysed at least once a day.

During unsteady plant operating conditions it will be necessary to increase the frequency of pH measurements. In particular if the AN solution is to be stored for a long period of time, e.g. during a plant shut-down, care should be taken to ensure that the monitoring of process conditions such as pH, temperature and concentration is continued.

NO_x and/or N_2O monitoring

On-line monitoring of these decomposition gases is an option for the early detection of decomposition.

Contamination

Regular analysis of the AN solution should be carried out to check for the required purity and safety (see Sections 4.1 and 9).

Precautions should be taken during operation and maintenance activities to prevent contamination of the storage facility. In particular, contamination of hot ammonium nitrate solution with oil (e.g. in the pumping area) is potentially dangerous.

Where there is a risk of accumulation of insoluble matter on the surface of the solution e.g. due to the presence of contamination in the feed streams, provision should be made for sampling the solution from the surface and the removal of any contaminated layer according to written procedures. The sampling should be done regularly depending on the nature of the process.

The storage area should be kept tidy and free from all rubbish.

5.3. Operation Under Upset Conditions

In situations where a decomposition is detected but an intervention is not possible, emptying the tank and containing the run-off may be considered. The risk of a runaway decomposition is thereby reduced because no pressure build up can take place. The ammonium nitrate solution will cool down and to some extent solidify and can be maintained without contamination of surface/ground water or soil. A safe collecting area should be provided.

Instructions for operators should be in place stating how to bring the AN-storage tank back to normal condition following upsets.

The typical main deviations are as follows:

- Temperature: high and low
- pH: high and low
- Level: high and low
- Contamination
- Blockage in the line and lack of circulation (i.e. no flow condition)
- Leakage
- Pressure: high and low

Temperature

High temperature conditions can arise as a result of e.g. AN solution feed at high temperature, malfunctioning of the heating system and decomposition.

In a high temperature situation **one or more** of the following actions may be taken:

1. Isolate the heat input e.g. trip shut steam valve
2. Stop the AN solution feed

3. Add water (see details below)
4. Add ammonia e.g. in the event of a decomposition

Low temperature conditions can arise as a result of e.g. cooler AN solution feed, loss of heating, inadvertent addition or ingress of water.

pH

Low pH conditions can arise due to e.g. a malfunction of the pH control system in the AN production unit or a loss of ammonia during storage.

In the event of a low pH situation **one or more** of the following actions may be taken:

1. Add ammonia: normally a low pH is corrected by adding ammonia gas.
2. Mix with AN solution of a higher pH.

High pH conditions can arise due to e.g. a malfunction of the pH control system in the AN production unit. This is not an unsafe condition as the solution will tend to lose ammonia gradually during storage. However, this could be an environmental issue e.g. a problem with ammonia odour in the vicinity.

Level

High or low level conditions usually arise due to a malfunction of the level instruments or mal-operation.

High level situations can lead to the overflow of the AN solution from the tank. Such overflow should be appropriately directed to minimise environmental implications. A low level condition may cause cavitation in the solution pump and may also lead to the steam coil not being covered with AN solution. The operator should investigate and take appropriate action.

Contamination

The presence of contamination may be indicated or suspected in a number of ways:

1. Direct e.g. chemical analysis of the AN solution or visual inspection (e.g. suspended matter, coloration).
2. Chemical analysis of the raw materials.
3. Indirectly from the effects of the contamination on the solution e.g. temperature-rise, evolution of gases.

Appropriate action based on the nature and quantity of the contaminant must be taken in the event of the first two cases. In the third case, the consequential effects (e.g. temperature rise) need to be analysed by operators as there may be various possible causes.

If the consequential effects are likely to be associated with contamination, intervention measures must be taken to control the situation. These may include:

1. The isolation of AN solution feed
2. Identifying the source of contamination and prevention of further ingress
3. The isolation of the heat input
4. The addition of water (see details below).

Blockage in the line and lack of circulation

When a line gets blocked with crystallised AN, care must be taken to avoid heating the AN under confinement during any attempts to clear the blockage. Safe procedures must be followed which prevent this and the risk of personnel being sprayed and affected by the hot solution. Such procedures could involve, for example, opening up the line at one end and injecting hot condensate carefully to dissolve crystallised AN.

A potentially hazardous situation can arise in the pump due to lack of circulation as a result of line blockage and this can be detected by e.g. flow meter, pump low amps or temperature sensors. Under the no-flow situation the pump can overheat and may explode. Appropriate protection should be provided to avoid such a situation. In addition, the lack of circulation can also adversely affect the mixing of the AN solution in the tank.

Leakage

Leakages mainly occur from flanges and seals e.g. from the pump systems. Small leakages will lead to the solidification of the spilled ammonium nitrate but larger amounts may collect in pits and drains. These leakages should be properly managed.

Pressure

High pressure conditions may arise from decomposition gasses and from evaporated water in the course of intervention measures. Vents must be designed and installed for a credible worst case scenario (see Section 4.4).

Low pressure conditions can be avoided by the proper design of the vent system or vacuum relief valve, taking into account the highest possible off-take as well as a sudden cooling down of the vapour phase e.g. by the addition of cold water.

Addition of water in case of increasing temperatures

The addition of water can be initiated manually according to the operating procedures or may be triggered by an automatic trip/ interlocking sequence. The use of this intervention technique shall be described in the operating instructions. The addition of water shall occur after reaching a specified temperature value (5-10°C above a selected alarm temperature, see Section 4.4).

Water may be added in various ways: on the top of the liquid surface; by means of a dip pipe (normal or perforated); or by means of a jet system. The risk of blockage occurring in the water line due to crystallisation of AN should be considered and should be addressed, where necessary, for example, by the provision of a small continuous flow of water in the pipe/jet.

Whichever method of water addition is used, consideration should be given to the effectiveness of its mixing with the AN solution for controlling the reaction within the available time (see below).

The spraying of ambient temperature water into the free space above the liquid in the storage vessel is not a preferred option as it can present the risk of a rapid condensation of vapour, which can create a vacuum inside the storage tank possibly causing damage. The tank has to be provided with adequate vacuum relief capacity against this hazard.

Sufficient free space between the maximum filling level and the overflow position in the storage vessel should always be kept to accommodate any liquid swell which may be caused by the flash steam produced when water is added.

A reliable source for the dilution water is essential. Water can be provided from a static head tank, a local water network or a fire fighting water system. If a pump is used, a back-up power supply is recommended to safeguard against power failure. Water used for emergency actions should preferably be free from contaminants. However, in the selection of the water source, consideration should be given to the reasonable and reliable availability and the associated practical aspects.

Time available for response

The Time to Maximum Rate (TMR) depends on various factors, such as the type and quantity of contaminants as well as the AN concentration and solution temperature. In the EFMA study the kinetic rates of decomposition of AN solutions which were acidified and contained selected contaminants, were found to be relatively low in the typical operating temperature range 130-150°C. For example, the results of the Dewar experiments with predefined contamination levels (under fairly pessimistic scenario conditions: 94% AN solution at pH 2 and containing 100ppm chloride contamination), show that the time for the temperature to rise from about 160°C to the temperature corresponding to maximum rate is about 5-6 hours. This means that in industrial situations there would be sufficient time available to intervene during a decomposition reaction before it could develop into a dangerous escalation.

6. MAINTENANCE

6.1. Regular Cleaning and Inspection of Storage Tanks

Empty and clean the tank at regular intervals particularly removing any deposits (e.g. corrosion products) that may have collected at the bottom of the tank. Thoroughly inspect and carry out any required maintenance work. The cleaning of the tanks should be performed according to a written procedure and be recorded. Where appropriate, the deposits should be analysed in order to identify their sources and to eliminate them where practicable.

Care should be taken to avoid cavitation when the tank is emptied using a pump.

The tank is usually cleaned with water and organic solvents are not recommended. Contact between organic solvents and ammonium nitrate shall be avoided. The tank shall be rinsed with clean water before commissioning.

6.2. Mechanical Integrity and Repairs

Inspection of the tanks should cover aspects of mechanical integrity and corrosion in addition to other aspects.

Valves, safety valves and other equipment should be checked periodically. If the steam coil has sprung a leak, it should be repaired. The damaged sections should not be isolated so as to avoid trapping and confining ammonium nitrate in the coil.

It is good practice to avoid patchwork when carrying out repairs. The damaged area should be cut out and replaced by a flush-fitting piece of new material. This is to avoid double plating which could cause ammonium nitrate to be trapped between the plates and its subsequent heating by the hot solution when the tank is put back in service. As stated in 3.2, under such conditions of heating and confinement, AN can give rise to an explosion hazard.

7. SAFETY EQUIPMENT

The following safety equipment should be provided on the site:

- A supply of water under pressure with hydrants and hoses, protected against frost in winter.
- An appropriate number of showers and eye wash devices.
- Protective clothing with a face screen available to be worn by operators before making connections, breaking connections, or breaking joints.
- Face shield or goggles, gloves, safety shoes or boots and protective aprons available to operating personnel. Operating instructions should specify the use of personal protection equipment.
- Breathing apparatus or escape sets to safeguard against any emission of toxic fumes.

8. PERSONNEL TRAINING, FIRST AID AND EMERGENCY PLANS

All personnel involved in the storage of the solutions must be given training about the potential hazards of AN, safe procedures to use for operation and maintenance and the precautions and actions to take in the event of an emergency e.g. fire, emission of toxic fumes, skin burning by hot solution.

Information on how to act in an emergency can be found in the safety data sheet for ammonium nitrate solution (see Appendix 1).

Emergency plans for potential scenarios such as fire and toxic fume release should be prepared, kept in a written form and should be regularly practised. The relevant records should be kept.

9. REGULATIONS

Information concerning current regulations at the time of preparation of this guidance (2005) is summarised below. Readers are advised to check for any revision and consult the most up to date legislation.

Seveso Directive
AN solution containing more than 80% AN is listed as a hazardous substance in the Seveso Directive (Ref. 7 and 8)

Classification, Packaging and Labelling Directive
Ammonium nitrate solutions are not classified as hazardous material according to the amended EEC Directive 67/548/EEC (Annex 1B of Directive 2004/73/EC) (Ref. 9).

UN Transport Regulations
International transport regulations e.g. UN Orange Book (Ref. 10), European rail, RID (Ref. 11), European road, ADR (Ref. 12) and international sea, IMDG (Ref. 13) classify hot ammonium nitrate

solution containing more than 80% AN as an oxidizing substance, Class 5.1 UN No. 2426 (Ref. 10), with special provisions which specify the following safety related parameters:

- AN content not to exceed 93%
- to contain not more than 0.2% combustible material
- pH between 5 and 7 measured in an aqueous solution of 10% of the substance carried
- the maximum content of chloride ions should not exceed 0.02%

Readers are advised to consult the actual regulations for full and exact details.

10. REFERENCES

1. Safety Recommendations for the Storage of Hot Concentrated Ammonium Nitrate Solutions IFA/APEA Guidance 1985.
2. TNO report. Safety Aspects of ammonium nitrate solutions at high temperatures. November, 2003.
3. Shah, K. D. and Roberts, A. G., Chapters 11 and 15 in Nitric Acid and Fertiliser Nitrates. Fertiliser Science and Technology series. Volume 4 ed. C. Keleti, published by Marcel Dekker. ISBN 0-8247-7332-2.
4. Shah, K. D., (1996) Safety of Ammonium Nitrate Fertilisers. Proceedings 384, The International Fertiliser Society, York, UK
5. Guiochon, G., Thermal decomposition of pure ammonium nitrate, catalytic effects of various inorganic compounds Annals Chim. 5, (1960), 295-349
6. Bauer, A., King, A., and Heather, R. (1982). The Explosion Hazards of Ammonium Nitrate and Ammonium Nitrate Based

Compositions – A Summary. A report published by the Department of Mining Engineering, Queen's University, Kingston, Canada.

7. Council Directive 96/82/EC of 9 December 1996 on the control of major-accident hazards involving dangerous substances. Official Journal of the European Community L 010, 14.1.97 pages 13-33.
8. Directive 2003/105/EC of the European Parliament and of the Council of 16 December 2003 Amending Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances. OJ L345/97 31.12.2003. Pages 97-105.
9. Commission Directive 2004/73/EC of 29 April 2004 adapting to technical progress for the twenty-ninth time Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. OJ L 152 of 30.04.2004.
10. UN Recommendation on the Transport of Dangerous Goods: Model regulations. 13th revised edition, 2003. United Nations Publication ISBN 92-1-139090-7.
11. Convention concerning International Carriage by Rail (COTIF). Appendix B. Uniform Rules concerning the Contract for International Carriage of Goods by Rail (CIM). Annex I Regulations concerning the International Carriage of Dangerous Goods by Rail (RID). 2003 Edition. ISBN 0115522654.
12. European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR). Edition 2003. Volumes I and II. United Nations Publication ISBN 92-1-139090-7.
13. International Maritime Dangerous Goods Code (IMDG) 2002 Edition. ISBN 92-801-51-40-1.

APPENDIX 1

Safety Data Sheet
AMMONIUM NITRATE SOLUTION

1. IDENTIFICATION OF THE PRODUCT AND THE COMPANY

1.1. Identification of the Product

Designation	Ammonium nitrate, hot solution in water (80-93%)
Trade name	
Commonly used synonyms	
EINECS Name	Ammonium nitrate solution (80-93 weight %)
Intended use	Raw material for production of fertilizers, explosives and nitrous oxide

1.2. Company

Address	Telephone No. Telefax No. Telex No.

1.3. Emergency calls

Company	Telephone No.
and/or	
official Advisory Body	Telephone No.

2. COMPOSITION/INFORMATION ON INGREDIENTS

2.1.

CAS Number	6484-52-2
EINECS Number	229-347-8
Molecular formula	Main ingredient NH_4NO_3

2.2. Nature of ingredients and concentration

Hot concentrated solution of ammonium nitrate in water, x% AN.

2.3. Classification

Not classified as hazardous material according to EEC Directive 67/548/EEC (as amended last by EC Directive 2004/73/EC).

3. HAZARDS IDENTIFICATION

3.1. Human health

These solutions are dangerous because of their high temperature and because they attack the skin on account of their oxidizing properties.

Skin Contact

- Hot material will cause thermal burns.

Eye Contact

- Hot splashes will cause eye burns and permanent eye damage.

Ingestion

- This event is most unlikely because of high temperature of product.
- However, small quantities of ammonium nitrate are unlikely to cause toxic effect. Large quantities may give rise to gastro-intestinal disorders and in extreme cases, formation of methaemoglobin (blue baby syndrome) and cyanosis (indicated by blueness around the mouth) may occur.

Inhalation

- Mists and low concentrations of ammonia released from the hot solution may cause irritation of eyes, nose, throat and upper respiratory tract.

Long term effects

- No adverse effects are known.

Fire and thermal decomposition products

- Inhalation of decomposition gases, containing nitrogen oxides and ammonia, can cause irritation and corrosive effects on the respiratory system. Some lung effects may be delayed.

3.2. Environment

Ammonium nitrate is a nitrogen fertilizer. Heavy spillage may cause adverse environmental impact such as eutrophication in confined surface waters or nitrate contamination. See Section 12.

3.3. Other

Fire, heating and detonation

- When strongly heated, concentrated ammonium nitrate solutions may decompose giving off nitrogen oxides and ammonia.
- Decomposition may start if the solutions become acidic (this is catalysed by Cl, Fe, Co Ni, Cr, Zn and Cu), but can be arrested by correcting the acidity by the addition of gaseous ammonia. Heating under strong confinement can lead to explosive behaviour. Addition of alkaline materials may cause evolution of ammonia vapours.

4. FIRST-AID MEASURES

4.1. Product

Skin Contact

- Do not remove contaminated clothing.
- Flush skin immediately with large amounts of cold water.
- If possible, submerge affected area in cold water and pack with ice.
- Obtain immediate medical attention.

Eye Contact

- Flush/irrigate eyes with copious amounts of water for at least 10 minutes.
- Obtain immediate medical attention.

Ingestion

- This event is most unlikely because product is hot.
- In case of ingestion, do not induce vomiting.
- Wash out mouth with water and give 2 or 3 glasses of water to drink.
- Obtain immediate medical attention.

Inhalation

- Ingress of hot solution by inhalation is most unlikely, however, if toxic vapours are inhaled:
- Move the injured person to fresh air at once.
- Keep the patient warm and at rest.
- Administer oxygen, especially if the person is blue in the face.
- Apply artificial respiration, if breathing has stopped.
- Obtain immediate medical attention.

4.2. Fire and decomposition products

Inhalation

- Move the person from the source of exposure to fumes.
- Keep warm and at rest even though no symptoms may be evident.
- Give oxygen, especially if the person is blue in the face.
- Apply artificial respiration, if breathing has stopped.
- Obtain medical attention immediately.
- Following exposures, the patient should be kept under medical review for at least 48 hours as delayed pulmonary Œdema may develop.

5. FIRE-FIGHTING MEASURES

The product is not combustible, but it will support combustion even in absence of air.

5.1. If fertilizer is not directly involved in the Fire

Use the best means available to extinguish the Fire.

5.2. If fertilizer is involved in the Fire

- Call the Fire brigade.
- Avoid breathing the fumes (toxic). Stand up-wind of the Fire.
- Use a self-contained breathing apparatus if fumes are being entered.

- Use plenty of water to smother the Fire.
- Cool Fire-exposed containers and structures with water spray.
- If water containing fertilizer enters any drains or watercourse, inform the local authorities immediately.

6. ACCIDENTAL RELEASE MEASURES

6.1. Personal Precautions

- Put on protective equipment before entering danger area. (See Section 8)
- Keep combustible materials (wood, paper, oil, etc.) away from spilled product.

6.2. Environmental Precautions

- Take care to avoid the contamination of watercourses and drains.
- Inform appropriate authority in case of accidental contamination of watercourses.

6.3. Methods for Cleaning

- Swill away small spillage with copious quantities of water.
- Contain large spillage with sand or earth as necessary.
- Allow material to solidify and scrape up.
- Place material in suitable containers for recycle or disposal.

7. HANDLING AND STORAGE

7.1. Handling

- Wear eye and hand protection.
- Provide adequate ventilation.
- Avoid contamination, especially with incompatible materials. (See Section 10.3)

7.2. Storage

- Locate the tanks away from any storage of incompatible substances. (See Section 10.3)

- Protect the tanks from corrosion and physical damages.
- Keep solutions above crystallisation temperature to prevent precipitation but they should not be allowed to exceed 150°C. (In transport 140°C as per IMDG Code).
- Check pH of the solution daily. If the pH of a 10% aqueous solution is below 4.5, gaseous ammonia should be added to raise it above 4.5.
- Suitable material for tanks is austenitic stainless steel.
- Do not permit smoking and use of naked lights in the storage areas.

8. EXPOSURE CONTROL/PERSONAL PROTECTION

8.1. Occupational Exposure Limits
No official specific limits.

8.2. Precautionary and Engineering Measures
- Avoid exposure to vapours and provide local exhaust ventilation where necessary.
- Provide safety showers and eye washing facility at any location where skin or eye contact can occur.

8.3. Personal Protection
- In emergency situations, use suitable respiratory protection.
- Wear heat resistant gloves and protective clothing.
- Use chemical safety goggles or full face shield.

9. PHYSICAL AND CHEMICAL PROPERTIES
% concentration figures below refer to ammonium nitrate content.

Appearance	Colourless clear liquid when free from crystals
Odour	Weak ammonia odour
pH water solution (conc. 10% AN)	> 4.5 (for transport, pH must be between 5 and 7)

Freezing point	96° C at 90% AN, 110° at 93% AN
Boiling point	146° C at 90% AN; 159°C at 93.0% AN
Vapour pressure at 100°C	39.6kPa (80% AN); 22.6kPa (89.9% AN)
Oxidizing properties	Not classified as an oxidizing material according to Directive 67/548/EEC
Explosive properties	Heating under confinement can lead to a violent reaction or explosion. Not classified as explosive
Solubility in water	Miscible in all proportions
Density	1.41g/cm^3 at 100°C (91% AN)
Partition coefficient, n-octanol/water	-3.1 (AN at 25°C pH 6; OECD guidelines 107)

10. STABILITY AND REACTIVITY

10.1. Stability

The product is stable when properly stored, handled and used.

10.2. Conditions to Avoid

- Temperatures below crystallisation point and above 150°C (decomposition).
- Maximum temperature 140°C in transport – IMDG Code.
- Acidification of solutions.
- Dewatering of solutions.

10.3. Materials to Avoid

Contact with combustible materials, reducing agents, acids, alkalis, soda ash, chlorides, chlorates, chromates, nitrites, metals such as copper, iron, cobalt, nickel, zinc and zinc alloys.

10.4. Hazardous reactions/decomposition products

Concentrated ammonium nitrate solutions react with organic materials (e.g. wood, oil or grease) in some situations after some time delay. They react vigorously with zinc and zinc alloys (see Section 3.3).

11. TOXICOLOGICAL INFORMATION

11.1. General

See Section 3.1.

11.2. Toxicity Data

LD50 (oral, rat)	2460-2950mg/kg (OECD Guideline 401)
Local effects	Ammonium nitrate itself is not classified as irritating. For hot solutions see Section 3.1
Sensitization	No known adverse effects
Chronic or long-term effects	No known adverse effects
Special effects	Ingestion of large quantities of AN may induce methæmoglobinæmia (See Section 3.1.)

12. ECOLOGICAL INFORMATION

12.1. Mobility

Very soluble in water. The NO_3^- ion is mobile. The NH_4^+ ion is adsorbed by soil.

12.2. Persistence/Degradability

The nitrate ion is the predominant form of plant nutrition. It follows the natural nitrification/denitrification cycle to give nitrogen, the product is biodegradable.

12.3. Bio-accumulation

The product does not show any bio-accumulation phenomena.

12.4. Ecotoxicity

Low toxicity to aquatic life.

Ammonium nitrate (pure)	LC50-48h fish *(Cyprinus carpio)*: 74-102mg/l IC50 invertebrates *(Daphnia magna)*: 555mg/l IC50 algae *(Scenedesmus quadricauda)*: 83mg/l

(Source IUCLID)

TLM 96 between 10-100ppm

13. DISPOSAL CONSIDERATIONS

13.1. General

Disposal should be in accordance with local or national legislation.

14. TRANSPORT INFORMATION

14.1. UN Classification

Class 5, Division 5.1 Oxidizing Substances, UN No 2426.
Shipping name: AMMONIUM NITRATE, LIQUID

14.2. Details

Composition	UN No.	Class	Transport Mode Particulars	Label
≤93% AN ≤0.2% combustible ≥7% water ≤0.02% Cl- ions pH 5-7	2426	5.1	IMDG: Packaging gr.: Tanks only Stowage cat.: D Max. allowable transport temperature: 140°C	5.1
>80 and ≤93% pH 5-7	2426	5.1	ADR/RID	5.1

15. REGULATORY INFORMATION

15.1. EEC Directives

- 2003/2003/EC (Law relating to fertilizers)
- 96/82/EC as amended by 2003/105/EC (Seveso Major Accident Hazard)

15.2. National Laws

16. OTHER INFORMATION

R phrases: None

Further information available in the guidance published by European Fertilizer Manufacturers' Association (2005): *Guidance for the Storage of Hot Ammonium Nitrate Solutions.*

The information in this safety data sheet is given in good faith and belief in its accuracy based on our knowledge of the substance/preparation concerned at the date of publication. It does not imply the acceptance of any legal liability or responsibility whatsoever by the Company for the consequences of its use or misuse in any particular circumstances.

Date of issue: Date of revision:

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