Bulk fertilizer cargos: Safety aspects of transfer operations at ports

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Summary

Millions of tonnes of substances (raw materials and products) are transported in bulk by sea across continents for the fertilizer industry. Some of the materials are classified as dangerous for transport. This article considers their nature, potential hazards and classification. It describes various precautions to take to minimise safety and environmental risks.

Introduction

The fertilizer industry is a global and large tonnage industry, requiring shipments of large quantities of raw materials and finished products across continents. This is because fertilizers are essential for crop production and agriculture, and the source materials for the three main plant nutrients viz. nitrogen, phosphate and potassium are not available naturally in all regions.

In modern manufacturing processes nitrogen is obtained from air to produce ammonia, the process requiring natural gas or other similar hydrocarbons as the main raw material. Ammonia is then used to produce ammonium nitrate (AN) and urea, which are widely used main nitrogen fertilizers. The main source of phosphate (commonly expressed as P_2O_5) is rock phosphate mineral, which is processed to produce phosphoric acid. Ammoniation of phosphoric acid enables production of mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP); whereas acidification of the rock can give single super-phosphate (SSP) and triple super-phosphate (TSP). These materials are the common sources of P_2O_5. Lastly, potassium (expressed as K_2O) is mainly sourced from potassium chloride, described in the industry as potash, which is mined. Other source materials are also used for the above nutrients, for example, ammonium sulphate (AS), potassium nitrate, potassium sulphate, calcium nitrate and sodium nitrate.

Fertilizers, which contain more than one nutrient, are known as Compound or NPK (NK or NP); they are produced by combining some of the above materials. Thus, the fertilizer industry is involved in transporting by sea millions of tonnes of these substances in bulk (i.e. in unpackaged form).

This article focuses on the safety and environmental aspects of loading and unloading bulk materials at ports.

Potential hazards

General

The main substances of interest as regards to potential physicochemical hazards are those based on ammonia and/or nitrate (NO_3^-) ion; ammonium salts being relatively unstable at elevated temperatures and nitrate being oxidizing in nature. Thus, products which deserve attention mainly include (AN) and those based on AN, potassium nitrate, ammonia and ammonium salts (MAP, DAP, urea).

Potential hazards

AN possesses oxidizing properties and, as such, can react with most combustible materials. When heated, it undergoes thermal decomposition, which is complex as it involves a combination of a number of irreversible exothermic reactions and an endothermic vapour-pressure-dependent reversible dissociation. Run-away reactions are not common with AN as they require conditions of high temperature, pressure and/or contamination. In these reactions toxic gases such as NOx are given off. A number of substances such as chloride, chromates, Cu and Zn, have a catalytic effect on the decomposition.

The oxidizing properties of AN give rise to the potential fire hazard in the presence of combustible materials. Other nitrates e.g. potassium nitrate, also do like-wise.

Pure AN is difficult to detonate; normal friction, spark and impact are incapable of initiation. Fertilizer grade AN, which is in the form of high density prills or granules, is particularly difficult to detonate. Change in the physical form and/or presence of reactive contaminants lower the resistance to detonation.

Some fertilizers based on AN and potash (a chloride source with catalytic effect on AN decomposition) can exhibit the so-called self-sustaining decomposition (SSD) capability. They can continue to decompose exothermally once initiated by a hot source, even after the source is removed. The associated release of toxic fumes is a significant potential hazard.

Ammonium salts e.g. MAP, DAP, urea and AS, are capable of releasing ammonia gas when heated e.g. in a fire; but would require much heat input; they are not classified as dangerous in transport regulations.

Ammonia, a major raw material for the fertilizer and many other industries, is transported in large quantities in ships mostly in refrigerated form. Ammonia vapours are toxic and liquid ammonia can cause severe cold burns. Although ammonia gas is flammable within certain range of concentrations; it is very difficult to ignite and does not readily sustain combustion in outdoor situations.

Environmental hazards

Most of the solid fertilizer raw materials and products are not considered as hazardous to the aquatic life. Although ammonia itself is toxic to marine life; its salts are much less so for the reason that it is the free ammonia dissolved in water which is toxic and not the ammonium ion, NH_4^+. Nitrates are also not particularly harmful to the aquatic life during short exposures which may result as a consequence of a sudden loss of containment. (Long term low level exposure is a different issue and is not relevant here.)

Classification

Based on the hazardous properties described above a number of fertilizer materials are classified as dangerous in the transport regulations viz. Orange Book which describes the Transport of Dangerous Goods Model Regulations and the International Maritime Dangerous Goods Code (IMDG) 2002 (see Table 1).

For bulk transport of AN-based fertilizers by sea there are two special requirements specified in the BC Code of Safe Practice for Solid Bulk Cargoes as written by the International Maritime Organization (IMO). For fertilizers belonging to UN number 2067, the Resistance to Detonation test, D.5, must be carried out and the product must pass the test. This test is designed to show that the fertilizer has high resistance to detonation and thus the risk of mass destruction from it is very low. It is pertinent to note

TABLE 1: TRANSPORT REGULATIONS

UN number	Product	Class	Subsidiary risk	Packing group
Ammonia related entries				
1005	Ammonia anhydrous	2.3	8	
3318	Ammonia solution, relative density less than 0.880 at 15°C in water, with more than 50% ammonia	2.3	8	
2073	Ammonia solution, relative density less than 0.880 at 15°C in water, with more than 35% but not more than 50% ammonia	2.2		
2672	Ammonia solution, relative density between 0.880 and 0.957 at 15°C in water, with more than 10% but not more than 35% ammonia	8		III
Ammonium nitrate and other nitrates related entries				
2067	Ammonium Nitrate Based Fertilizers: Defined in special provisions 306 and 307 (see below)	5.1		III
2071	Ammonium Nitrate Based Fertilizers: Defined in special provision 193 (see below)	9		III
1479	Oxidizing solid N.O.S.	5.1		I,II & III
1486	Potassium nitrate	5.1		III
1499	Sodium nitrate and Potassium nitrate mixture	5.1		III
2426	Ammonium nitrate Liquid (hot concentrated solution)	5.1		
3139	Oxidizing Liquid N.O.S.	5.1		I,II & III
Nitric acid				
2031	Nitric acid, other than red fuming,			
	– with <70% HNO3	8		II
	– with >70% HNO3	8	5.1	I

Class 2.2 *Non flammable, non-toxic gases*
Class 2.3 *Toxic gases*
Class 5.1 *Oxidizing substances*
Class 8 *Corrosive substances*
Class 9 *Miscellaneous dangerous substances and articles.*

Special Provision 306

This entry may only be used for substances that do not exhibit explosive properties of Class 1 when tested in accordance to Test Series 1 and 2 of Class 1 (see Manual of Tests and Criteria, Part I).

Special Provision 307

This entry may only be used for uniform mixtures containing ammonium nitrate as the main ingredient within the following composition limits:

(a) Not less than 90% ammonium nitrate with not more than 0.2% total combustible/organic material calculated as carbon and with added matter, if any, which is inorganic and inert towards ammonium nitrate; or

(b) Less than 90% but more than 70% ammonium nitrate with other inorganic materials or more than 80% but less than 90% ammonium nitrate mixed with calcium carbonate and/or dolomite and not more than 0.4% total combustible/organic material calculated as carbon; or

(c) Nitrogen type ammonium nitrate based fertilizers containing mixtures of ammonium nitrate and ammonium sulphate with more than 45% but less than 70% ammonium nitrate and not more than 0.4% total combustible/organic material calculated as carbon such that the sum of the percentage compositions of ammonium nitrate and ammonium sulphate exceeds 70%.

Special Provision 193

This entry may only be used for uniform ammonium nitrate based fertilizer mixtures of the nitrogen, phosphate or potash type, containing not more than 70% ammonium nitrate and not more than 0.4% total combustible/organic material calculated as carbon or with not more than 45% ammonium nitrate and unrestricted combustible material. Fertilizers within these composition limits are only subject to these regulations when transported by air or sea and are not subject to these regulations if shown by a Through Test (see Manual of Tests and Criteria, Part III, sub-section 38.2) not to be liable to self-sustaining decomposition.

that AN, typically of low density and porous in nature, is widely used for making ANFO (ammonium nitrate + fuel oil) blasting agent. This type of AN, although more sensitive to detonation, is also classified as 5.1 oxidizer; however, with a different UN number, 1942. This substance generally does not pass the above detonation test and is shipped in packaged form.

For AN-based fertilizer of UN 2071, a Trough test, which enables the speed of the decomposition to be measured, has been specified in the UN test manual. The IMDG regulations prohibit fertilizers with greater than 25 cm/hour speed to be transported in bulk by sea.

It is uncommon to ship nitric acid, hot AN solutions and ammonia solutions as bulk sea cargos; they are not considered here further. Urea-AN solution is transported and used in large quantities, particularly in the US; it is not classified.

Past accidents

AN-based fertilizers

The most notable accident involving a shipment of AN fertilizer happened in Texas City in 1947: Cargoes of wax-coated AN aboard two ships were involved in major explosions following fires, with fatalities in excess of 600 and much damage to property. The sensitive nature of the product (due to wax-coating), presence of incompatible cargoes and incorrect fire-fighting method are considered as possible causes. The lessons learnt from this and other relevant accidents led to a better understanding of the behaviour of AN and the development and establishment of safety guidelines.

The industry took much care in implementing the recommended safe practices. As a result there have been very few serious accidents involving fertilizer solid raw materials or products in sea transport in the last 50 years or so. A small number of fires or decomposition accidents have happened, which have been of a relatively minor nature involving limited decomposition or fire.

Ammonia

Ammonia being toxic in nature can cause serious injuries or even fatalities amongst those exposed to the gas. A loss of containment can occur during loading/unloading or at sea. To the authors' knowledge there has been no major incident with ammonia at sea. Several accidents, however, have happened involving the transfer operations (loading or unloading) resulting in the release of ammonia e.g. from hose, flange or loading arm and causing multiple fatalities in a number of cases.

Industry guidance for safe practices

General

The fertilizer industry, particularly in western Europe and USA, has taken a proactive role in promoting safety. For safe transportation of potentially hazardous products handled, the industry trade associations have published a number of guidance documents. For example, European Fertilizer Manufacturers' Association (EFMA) has published detailed guidance booklets for ammonia by rail (EFMA Guidance for Transporting Ammonia by Rail. 2005), nitric acid in tanks by road and rail (EFMA Guidelines for Transporting Nitric Acid in Tanks. 1998.) and solid fertilizers by sea (EFMA Guidance for Sea Transport of Ammonium Nitrate based fertilizers. 2004). It is noteworthy that EFMA has established an extensive Product Stewardship programme under which fertilizer producers promote safety throughout the distribution chain, based on the cradle-to-grave approach.

For the sea transport, a number of recommendations for good practice have been made. Most of these apply to nitrate-based (e.g. AN-based and KNO_3) fertilizers; but in the interest of safety it would be sensible to apply them to ammonia-based as well (e.g. MAP, DAP, urea).

When chartering, vessels should be assessed to satisfy official statutory requirements and company criteria, if any. The charter party and/or the voyage instructions should include reference to safety inspections, precautions relating to the specific risks from the product (e.g. toxic hazard, decomposition or fire) and communications to the port authorities, coastguards and charterers/suppliers of any emergency.

For loading, transportation and unloading the cargos, checklists should be used to ensure that all necessary safety precautions are taken e.g. inspection of cargo holds prior to loading and ship/shore safety requirements, as per IMO regulations, where appropriate, or industry guidance.

Prior to loading a ship, the ship master should be given relevant safety information such as product safety data sheet and emergency plans/actions relating to the product hazards.

AN-based, ammonia-based and nitrate-based fertilizers

For these products, with regard to their potential hazards described on page 1, the main safety principles applicable are:

- Avoidance of storage of combustible substances near fertilizers;
- Avoidance of storage of incompatible substances near fertilizers;
- Avoidance of cross contamination with remains of previous cargoes;
- Avoidance of cross contamination of next cargo with fertilizer;
- Avoidance of sources of heat likely to affect the fertilizer; and
- Avoidance of application of heat (e.g. welding) to any section which may have trapped/confined fertilizer.

Safety precautions and instructions concerning avoidance of heat sources should be given to the ship's master. Particular care should be taken to ensure that light bulbs do not get buried in the fertilizer heaps.

Equipment such as a compact shovel used for removing the bulk fertilizer and emptying the vessel's hold should be fitted with safety items such as a fire extinguisher, spark arrestors on the exhaust and a collecting device for leaked oil and grease. No refuelling of the shovel/loader should be permitted in the ship's hold.

The terminal operator, the port authority and the local fire services should collaborate in the development of an emergency plan. It is also very important that they operate in a coordinated way in controlling any incident or real emergency.

Terminals and ships storing/handling/carrying AN-based UN 2071 fertilizers should be equipped with high-pressure water lances (commonly known as Victor lance); they facilitate injection of water deep into a bulk heap of fertilizer in case of a decomposition incident.

These recommendations are described in detail in the EFMA guidance (Guidance for Sea Transport of Ammonium Nitrate based fertilizers.). The guidance and the checklists can be downloaded from the EFMA website http://www.efma.org (publications).

Anhydrous ammonia (UN 1005)

With anhydrous ammonia, the transfer operations between ship and shore are potentially more hazardous than the journeys at sea. Its loss of containment is of main concern as regards to personnel safety and impact on environment.

A comprehensive check list should be prepared as a part of the loading/unloading procedure to ensure all required operations are carried out correctly and without omission. An emergency shutdown system must be provided incorporating remotely operable shut-off valves as appropriate. Main precautions for safe transfer operations between ship and shore generally include:

- Use of solid arms e.g. Chicksan arms to connect lines on ship to pipes on the shore;
- Provision of ammonia detectors and an alarm system to give warning of a release;
- Provision of emergency telephone;
- Provision of emergency water spray;
- Use of adequate personal protective equipment and emergency escape or 30 minute air sets, as appropriate;
- Gradual chilling of refrigerated ammonia lines from storage to the jetty in preparation for loading;
- Testing the emergency shutdown system prior to connecting;
- Depressurisation of jetty pipe work and marine arm of any residual pressure from a previous operation;
- Testing connections for leaks prior to transfer, e.g. using nitrogen and soapy water;
- Cable (umbilical cord) connection between ship and shore to facilitate closure of emergency valves;
- Careful monitoring of ship's position and movement with regard to the safe envelope of solid arms' reach;
- Removal of liquid ammonia from jetty pipe work and arm by use of ammonia gas; and
- Close communications between the ship's officer and jetty technician.

As required, samples of ammonia should be taken. Discharge of residual ammonia from loading lines into water should be avoided or minimised. Regular checks and good maintenance of all equipment, relief systems and lines is important

Concluding remarks

The fertilizer industry has transported substantial quantities of solid bulk fertilizer materials safely world wide without serious incidents over the last five decades thanks to the regulatory controls and industry guidance.

The safety record is not as good with ammonia shipments as serious incidents have occurred during transfer operations. Strict adherence to sound safety practices is required, both in maintenance and operation.

Disclaimer: The information and guidance provided in this article is given in good faith. The authors and their organisations accept no liability for any loss or damage arising from their use.

ABOUT THE AUTHORS AND THE ORGANISATION

Mr Shah was with ICI-Agricultural Division on Teeside (UK) for more than 25 years and then with Terra Nitrogen, which took over ICI's fertilizer business. He was Technical Director when he retired from Terra over a year ago. The work of Mr Shah has mostly focused on the safety of fertilizers, particularly ammonium nitrate (AN) and AN-based fertilizers. He has been actively involved in EFMA and has represented the industry at the UN for transport regulations over many years. He has published a number of papers and is currently President of the International Fertilizer Society. Mr Shah has been awarded an MBE by Her Majesty the Queen for his services to the fertilizer industry in the safety field.

Mr Van Balken worked for nine years at the Dutch Ministry of Fishery and Agriculture and then joined DSM, a multinational petrochemical company in the Netherlands in 1980. After starting in the Research Department, he worked in several managerial functions before finally becoming the head of the Department of Environment and Safety Research. In 1998, Mr Van Balken joined the European Fertilizer Manufacturers' Association where he is currently Director of Technology, Environment and Safety.

The European Fertilizer Manufacturers Association represents the major producers of mineral fertilizers in Europe. Its mission is to identify, support and manage the common interests of its members, to be the industry's voice and sounding board, and to provide members and stakeholders with a wide range of statistical information and studies. EFMA cooperates with supra-national organisations, in particular the institutions of the European Union, and is strongly committed to the principles of Responsible Care.

ENQUIRIES

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