ACCIDENTAL EXPLOSIONS INVOLVING AMMONIUM NITRATE: PHYSICO-CHEMICAL PROPERTIES, SAFETY,

INCIDENTS AND MITIGATION OF BLAST EFFECTS

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"The very material that was destined to create nourishment and bring life to millions … has suddenly proven to be a savage foe, for reasons we do not yet know."

Carl Bosch co inventor invertor of the Haber/Bosch Ammonia process after the Oppau explosion in 1921 [D Jeffreys(2010)]

INTRODUCTION

Ammonium nitrate (AN) is frequently the oxidizer of choice in commercial explosives and provides the nitrogen content of many fertilisers. It is produced in an exothermic reaction between ammonia and 60% nitric acid and is sold as solution of less than 92% strength or, as a solid, prill or granule, of high or low density. Accidents associated with ammonium nitrate are well known and are listed on a designated Wiki page [Wikipedia Ammonium Nitrate disasters, Shah (1996, 2002)]. Its properties have been extensively reviewed elsewhere [Kiiski (2009), Shah & Roberts (1985), Braithwaite (2008)].

AN is used extensively in fertilizers, commercial explosives and propellants. Pure solid AN will not readily deflagrate [Sinditskii (2005)] and unconfined detonation, via shock initiation, is only stable at large diameters. In the absence of contamination AN is not reactive to the vast majority of materials in the solid state i.e. at temperatures less than 169 ^{0}C.

Public perception of hazards associated with AN will have been influenced by recent events, notably the 2001 Toulouse explosion and the 2013 accident in West, Texas in 2013. The conclusions of enquiries into these particular accidents are not yet available. However, there are a large number of reports and investigations into ANincidents [Wikipedia Ammonium Nitrate disasters]. These allow us to categorize these events in four categories:

(i) In process events i.e. deviations from normal operations in process equipment e.g. Port Neal (1994)
(ii) Pre-1950 contaminant based incidents due to shock/ impact/fire prior to the regulation of organic content, anti-caking agents and contamination levels e.g. Oppau (1921) Texas City (1946)
(iii) Fire initiated incidents post 1950; e.g. West, Texas (2013)
(iv) Post-1950 incidents involving extreme contamination; e.g. Toulouse (2001)

Incidents such as these, as well as associated security concerns, have resulted in increasing regulation of AN storage. In the last decade the issue of absolute size of and separation distance for storage has gained more prominence in some jurisdictions. However, when closely examined, most regulations still depend on a risk analysis based on the likelihood of an explosion. The primary safety measures for AN still rely on eliminating contamination, fire risk and the possibility of shock impact. The focus on this paper will be on pure (<0.2 w/w % impurities) AN in solid or in aqueous solution: molten or contaminated AN is normally very hazardous material.

AN PROPERTIES

The relevant physical and chemical properties of AN are well established [King & Bauer(1978), Shah(1985), Van Dolah(1996), V van den Hoogenband (2008)] and are only summarised here. Pure AN is a white crystalline solid at ambient conditions and is a well-known oxidizer: in the absence of contaminants, overheating and major explosive shock it is unreactive i.e. whilst remaining in the solid state. It has a high minimum deflagration pressure and an initial endothermic reversible reaction on melting. Because of competing endothermic (reversible) and exothermic (irreversible) chemical pathways, it has a self-sustaining minimum temperature for reaction at different pressures, well in excess of its melting point temperature in the absence of an external heat source or strong confinement. The solid is hygroscopic and, can agglomerate. These properties will hold for the normal legally acceptable maximum levels of 0.2 % w/w organic content [Peddie (2013)]. Different prill types are available according to porosity/ density e.g. TGAN (Technical grade) and FGAN (fertiliser grade). Differences in physical form may affect some test results but have no effect on the basic physical properties.

Reaction Chemistry

The following are the primary reaction pathways, normally from the molten state though heats of reaction here are based on solid state standard pressure and temperature values.

$$NH_4NO_3(s/l) \;=\; NH_3(\mathrm{g}) \;+\; HNO_3(\mathrm{g}) \qquad -\ \Delta H = 186\ \mathrm{kJ/mole\ AN} \quad (1)$$

followed by a number of exothermic reactions e.g.

$$NH_4NO_3(s/l) \;=\; N_2O(g) + 2H_2O(g) \qquad -\ \Delta H = -37\ \mathrm{kJ/mole\ AN} \quad (2)$$

and at higher temperatures still

$$2NH_4NO_3(s/l) \;=\; 2N_2(g) + 4H_2O(g) + O_2(g) \qquad -\ \Delta H = -118\ \mathrm{kJ/mole\ AN} \quad (3)$$

AN Self Sustaining Reaction and Thermal Explosion

The two major competing reactions (1) and (2), shown above, at lower temperatures (> 250-300 ^{0}C) govern this process – once the solid AN has acquired its heat of fusion and become molten. Energy conservation principles and supporting experiments establish minimum temperatures for sustained reaction at any given pressure for an unconfined inventory i.e. where the reversible evaporation is not constrained [Feick & Heiner (1954)]. These temperatures are also affected by boundary conditions as in conventional thermal explosion theories

$$P = \left[1 + \frac{3}{2} \frac{\Delta H_R}{Q - \Delta H_I} \right] p$$

where $P, \mathrm{p}, \Delta H_R, \Delta H_I$ and Q are the total pressure, vapour pressure of ammonium nitrate, heat of the endothermic reversible reaction to HNO_3 and NH_3, heat of the primary irreversible reaction and the heat supplied from any external source per mole of decomposed AN respectively.

For atmospheric pressure in an adiabatic system the self-stabilization temperature, which would therefore preclude a thermal explosion, can be shown not to exceed 290 ^{0}C subject to there being no constraint to vaporization.

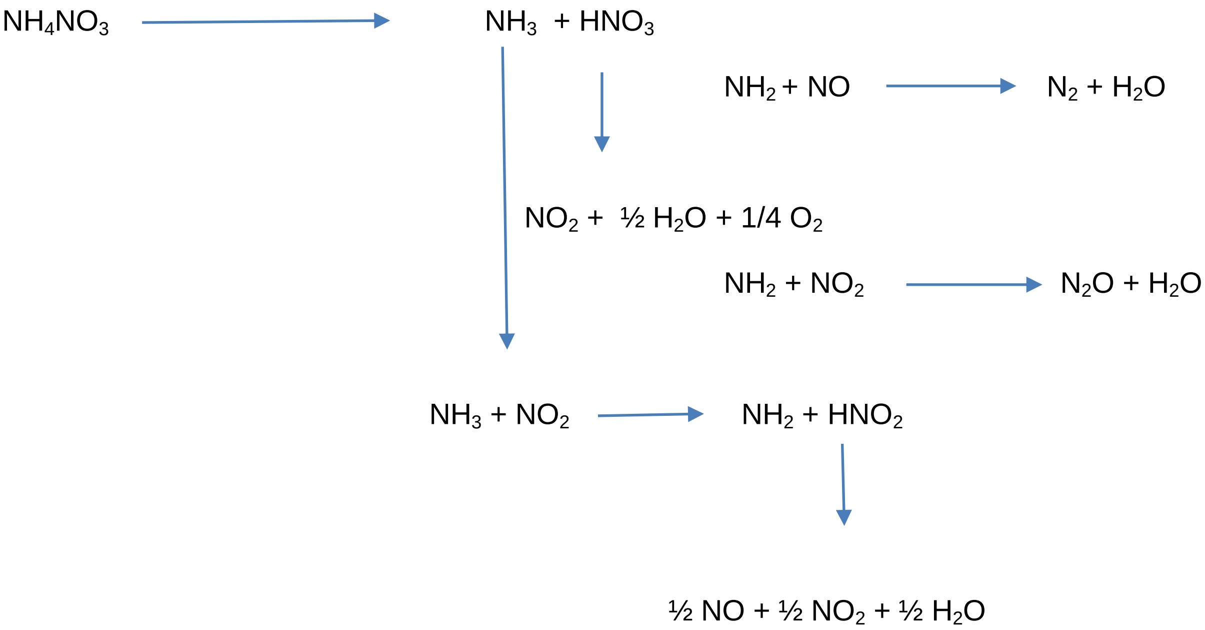

Figure 1 Simplified Mechanism for dissociation of AN {after Kiiski (2009)]

AN Deflagration

Minimum burning (or deflagration) pressures [ex Turcotte et al (2013)] have been measured for AN containing systems e.g. slurries, emulsions and NPK fertilizers. For the case of pure AN in the solid state these pressures are in excess of 0.1 GPa [Sinditskii (2005)] and this therefore precludes any deflagration or DDT process in normal working conditions. AN solution would require the water to be driven off before reverting to solid/ molten AN behaviour. This process may require a large amount of external fuel. In terms of deflagration properties some NPK mixed fertilizers containing ammonium nitrate can be categorized as “cigar burners”: it is to be noted these materials are not pure AN as they contain potassium chloride.

AN Shock and Shock to Detonation

Laboratory investigations and industrial accidents have demonstrated that under certain conditions pure solid AN can be detonated. It is a tertiary explosive, and as such, one which requires a combination of shock/ high velocity impact stimulus and large diameter and/ or heavy confinement to detonate.

INSULTS/ DEVIATIONS

The comparatively unreactive nature of pure solid AN can be dramatically changed by a variety of possible excursions from the normal (design) condition. These include the following (multiple deviations tending to synergism):

. Contamination (organic material, transition metals and salts, halide containing species, acidic conditions, reducing agents)

Rendering the inventory far more reactive/ energetic and bring the onset at lower temperatures .

Overheating resulting in molten AN

Possible leading to thermal explosion/ loss of containment (but still requires external stimulus)

. Severe shock/high velocity impact

Shock to detonation transition (SDT) under certain circumstances

. Gassing (solution)

Resulting in a solution potentially more susceptible to shock, Shock to Detonation (SDT)

In the continued and assured absence of such excursions, be they accidental or deliberate, it is hard to justify on purely technical grounds plant/ storage separation distances based on a solely thermodynamic analysis of AN explosive energetics. The AN accident history (Appendix A) suggests it is difficult to give cast iron assurances.

ACCIDENTS

Incidents involving AN have been reviewed in detail elsewhere [ex. Shah (1996), Braithwaite (2008), Wiki (2013)]. Appendix A lists a number of incidents involving AN. Incidents with NPK fertilizers, AN based secondary explosives or events resulting solely in pollution have been omitted.

Incidents caused by shock or high velocity impact, denoted by S have involved intimate contact between and explosive charge and the AN inventory. This is the result of attempts to de-agglomerate AN prills (before coating was standard practice) or by a high explosive charge detonation in or adjacent to an AN inventory. As with emulsion explosives, pumping operations with AN solution or melt pose a hazard and accidents have happened as a result of overheating in pumps (deadheading or dry running).

Almost without exception all of the remaining accidents appear due to a combination of overheating in a confined or semi-confined medium and faster exothermic chemical reaction facilitated by contamination. In these events, AN will have become molten before reacting.

(a) In process events i.e. deviations from normal operations in process equipment e.g. Port Neal (1994)
(b) Pre-1950 contaminant based incidents due to shock/ impact/fire prior to the regulation of organic content, anti-caking agents and contamination levels e.g. Oppau (1921) Texas City (1946)
(c) Fire initiated incidents post 1950; e.g. West, Texas (2013)
(d) Post-1950 incidents involving extreme contamination; e.g. Toulouse (2001)

Overheating/ contamination has occurred at an unacceptable frequency worldwide (Appendix A). It is not sufficient to cite freak accident although a number of accidents have shown clear regulatory breaches. . The recent major incidents at Toulouse and West, Texas, are either under investigation or legal curfew at the time of writing this paper. It has been suggested in the case of the former that contamination was a contributory cause.

Q-D RELATIONS: TNT EQUIVALENCE - RISK – DOMINO EFFECTS

TNT equivalence is routinely used for estimating minimum separation distances between explosive (non AN) inventories, ensuring unacceptable overpressures are not experienced elsewhere on or off-site. These analyses, in the strictest sense, apply to instantaneous events with a point source. With a secondary or tertiary explosive there is uncertainty as to the extent and efficiency of any reaction and a variety of factors have been introduced for the partial reaction in AN. Distances calculated can be much reduced by mitigating the consequences of any event (see below).

As can be seen from the Texas City accident (1947), domino effects (e.g. other storage or processing plant can be damaged by an initial explosion by means of fire, shock or shrapnel) have a greater effect on the consequences of the incident. It is clear from incidents involving disaggregation and those involving waste munitions that shock-to-detonation transitions (SDTs) are possible in large inventory AN media.

APPROACHES TO EXPLOSION MITIGATION

If a basis of safety cannot discount thermal, shock or contamination insult then there remains some measures that might mitigate against the worst consequences of an explosion. The results of an AN incident may include fire, shock and overpressures, shrapnel, rarefactions and toxic release to ground or atmosphere. The effects of explosions may be compounded by domino effects (sympathetic events initiated by a first explosion) on a production or storage site.

The consequences of any AN event might be mitigated by the following:

Compartmentalization – individual silos

Limiting the amount that can detonate in any single event

Overpressures are not additive for disparate events, nor is the kinetic energy of shrapnel. Consequences are therefore reduced at the cost of increased risks due to greater number of storage units.

Secondary containment/ bunkering – secondary/ tertiary containment

Reducing the probability of release outside the confines of the plant of shrapnel and overpressures by secondary containment (bunkering, barricades)

Secondary containment, if practical and cost effective, affords the option of limiting damage to a local storage or plant zone.

Fusible materials/ frangible seals – rapid release & avoidance of explosive LOC

Releasing or blanketing (water, alkali solution) contained inventory before loss of containment and reaction runaway

AN contains its own oxidant and fire fighting procedures based on oxygen starvation are not appropriate. Removing heat (as steam) or limiting reaction with ammonia is a possibility in some unconfined or partially confined scenarios.

Passivation/ stabilization of stored AN (inerting) e.g. inhibition by alkali/ ammonia

Storage by substitution (i.e. as separate ammonium and nitrate ions) is not likely to be a practical option. The injection of a stabilising medium, such as ammonia ensuring avoidance of acidic conditions, will limit the early decomposition of AN which is appropriate for liquid AN solutions. CAN (Calcium Ammonium Nitrate) fertiliser used in Europe are an example an example of alkali stabilisation. Often cited as giving resistance to detonation but , unfortunately, has little effect on this.

SUMMARY AND CONCLUSIONS

Based on risk analysis, the properties of AN in the absence of contamination or severe insult, support treating pure solid AN as an oxidizer. Whether this is a credible basis for reducing the need for substantial separation distances between AN storage, AN plants and the “outside world” is dependent on whether these insults can be eliminated and whether the assurances of the chemical, explosive and fertilizer industries that these deviations are controllable are accepted by the regulator and society in general. Regrettably the large number of incidents that have occurred, albeit from either human error or malicious act, encourage a more conservative approach.

In terms of take home messages, approaches to reducing AN hazards include:

(i) Elimination of sources of thermal, shock or mechanical stimuli (generally use non flammable construction material for stores)

(ii) Elimination of all possibility of contamination (generally do not permit **any** other materials to be stored with AN) and to

(iii) mitigating consequences of an event

(iv) Reduction of inventories/ compartmentalision & use calculated stand off distances

(v) Slowing AN reactions – alkaline conditions/ other passivators (The basis for CAN fertilisers)
(vi) Employing secondary confinement
(vii) Employing early detection methods and rapid quench/ rapid relief techniques

Convincing regulators and influencing public perception given the records of incidents involving AN is time consuming, but must be performed. We believe an open, transparent dialogue on AN risks will provide the best outcome for the industry.

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APPENDIX A

AMMONIUM NITRATE INCIDENTS (EXCLUDING EXPLOSIVES, NPK FERTILIZERS, ACUTE AND CHRONIC TOXIC EVENTS)

(1) In Process (C-contamination, Q-heat/fire, S-shock, D-Domino, ? uncertain)

January 1963, Finland – 10 fatalities – C, Q
A violent explosion occurred an 8 tonne molten AN mixing tank, possible due to high local concentrations of an organic anti-caking agent and failure of steam control system.

January 1969, Switzerland - C, (Q)
Contamination of 93 % w/w AN melt by $CaCl_2$ during maintenance led to an explosion and considerable damage. Contamination may have arisen as a result of a heat exchanger leak.

August 1972, Norway – C, Q
Explosion in a pump seal made of carbon, asbestos and organic fibre threads in plant handling 73 % w/w AN.

Cherokee Nitrogen Jan 1973
An explosion of around two tonnes of contaminated AN in a bulk store after a fire

January 1976, Canada - C
A minor explosion of an oil sump caused by migration of AN into the sump.

April 1978, Canada – C, (Q)
Rapid decomposition in a filter containing AN melt during steam cleaning operation. Organic contamination suspected.

August 1978, UK – Q, C
Rapid decomposition in a 92.5 % AN solution in a pump gland. Overheated by friction due to failure of water supply.

December 1994, Port Neal, Iowa USA – 4 fatalities - C
At about 6:06 am two explosions rocked the Port Neal, Iowa, AN processing plant operated by Terra Industries. Approximately 5,700 tons of anhydrous ammonia were released and releases of ammonia continued for six days after the explosions. Groundwater under the processing plant was contaminated by chemicals released as a result of the blast. The timing of the explosion occurred prior to the start of the arrival of the 8:00 am shift personnel, or the death toll may have been larger.

January 1998, Xingping, Shaanxi, China – 22 fatalities - ?
At midnight the Xinghua Fertilizer company had a series of explosions in the plant. About 27.6 tons of Ammonium nitrate liquor was in a container there. The explosion claimed 22 lives, with a further 56 wounded. The explosion was officially announced as an accident.

July 2009, Bryan, Texas, USA - ?

A plant El Dorado Chemical Company plant, which processes ammonium nitrate into fertilizer, caught fire at about 11:40 am. Over 80,000 residents in the Bryan/College Station area were asked to evacuate south of town due to the toxic fumes this fire generated.

(2) **Transport**

April 1925, Muscle Shoals, Alabama, USA – Q, C
Two carloads, each containing 220 barrels of ammonium nitrate, were dispatched and caught fire in transportation. The barrels had been stored in a warehouse with varying humidity for 6 years, so it is believed that they were ignited by friction with their nitrate-impregnated manila paper lining. Other shipments were reportedly more successful

April 1947, Texas City, United States - several hundred fatalities – C, Q, D
A cargo ship was being loaded when a fire was detected in the hold: 2600 tonnes of wax (rosin) coated AN in sacks were already aboard. The captain responded by closing the hold and pumping in pressurised steam. An hour later, the ship exploded and set fire to another vessel, 250 metres away and contained 1050 tonnes of sulphur and 960 tons of AN: this exploded the next day.

July 1947, Brest, France – 21 fatalities – Q, C
A cargo ship was loaded with 3300 tonnes of AN & various inflammable products when it caught fire. The vessel was towed out of the harbour and exploded.

1954, Red Sea – C, Q
A fire in a ships hold containing AN, paper & organics/ copper resulted in an explosion. The ship was abandoned.

August 1959 Roseburg, Oregon, USA – 14 fatalities – C, Q
A truck carrying dynamite and ammonium nitrate caught fire early in the morning. Several blocks of downtown Roseburg were destroyed.

1960, 1963 Traskwood, USA - Q, C
Wagons were derailed and a fire resulted. AN, nitric acid & hydrocarbons were involved in a fire & explosion.

1967 USA – Q, C
A fire involving 50 tonnes of AN in paper bags in wagons with wooden interior was allowed to burn out.

May, 1972 France – 2 fatalities - C
Suspected decomposition of lagging contaminated with AN & organics lead to an explosion in a road tanker carrying 22 tonnes AN solution (92.5 % w/w) and release of hot AN solution. Fire on contaminated insulation on road tankers (June, September)

August, 1972 Australia – 3 fatalities – Q, C
A fire in a semi-trailer with low density AN prills in bags lead to a detonation after 45 minutes.

January, 1973 USA – Q, C
A severe fire in a store near a plant holding 14,000 tonnes of high density AN prills, assisted by wooden structure and propane release from a fuel tank. Bulk heap of AN did not detonate

1997 Brazil - several fatalities – C, Q
AN truck fire compounded by fire in petrol tanker trying to pass. A detonation was thought to have been initiated by an exploding propane bottle. Fatalities were largely in a parked coach near to the fire.

2000 Florida, USA – one fatality – C, Q
Collision between an AN truck and gasoline tanker resulted in a fire. (Fatality due to collision).

March 2004, Barracas, Spain – 2 fatalities – Q, (C)
A truck carrying 25 tonnes of ammonium nitrate fertilizer exploded half an hour after a traffic accident on March 9, 2004, killing two people and injuring five others. The explosion, which could be heard at a distance of several kilometres caused a crater five metres deep.

May 2004, Mihailesti, Buzau, Romania – 18 fatalities – C, Q
A truck carrying 20 tonnes of ammonium nitrate tipped over on the European road E85 at 4:57 am. Shortly afterwards, a fire started in the cabin. Around 5:50 am the truck exploded, killing 18 and wounding 13 people. A crater 6.5 meters deep and 42 meters in diameter was formed by the explosion.

April 2004, Ryongchon, North Korea – 162 fatalities - ?
A freight train carrying ammonium nitrate exploded in this important railway town near the Chinese border. The train station was destroyed, as were most buildings within 500 metres, and nearly 8,000 homes were destroyed or damaged. Two craters of about ten metres in depth were seen at the site of the explosion. The authorities blamed "human error" for the explosion, although rumours persist that it was in fact an attempt to assassinate the North Korean leader Kim Jong-Il, who was due to be passing through the station at the time.

September 2007, Monclova, Coahuila, Mexico – 40 fatalities – Q, C
A trailer loaded with 22 tons of ammonium nitrate crashed into a truck leaving three dead in the crash. A fire then started in the trailer's cabin and approximately 40 minutes after that, a huge explosion occurred, resulting in around 150 people injured and 37 more dead. A crater 9.1 m wide and 1.8 m deep was created due to the explosion

(3) Disaggregation

July, 1921 Kriewald Germany (Poland) - 19 fatalities - S
Workers tried to dislodge 30 tonnes of ammonium nitrate which had aggregated in two wagons when blasting explosives were used the wagons exploded.

September 1921 Oppau, Germany – 509 fatalities - S
The fertilizer was a 50:50 mixture of ammonium nitrate & ammonium sulphate and the factory had used dynamite to disaggregate over 20,000 times without incident. It is thought that poor mixing had led to certain parts of the mass to contain more ammonium nitrate than others. Only 450 tonnes exploded, out of 4500 tonnes of fertilizer stored in the warehouse.

April 1942, Tessenderloo, Belgium - several hundred fatalities - S
An attempt to disaggregate a pile of 150 tonnes of ammonium nitrate with industrial explosives ended tragically.

(4) **Storage**

October, 1918 Morgan, New Jersey - S
One of the shells released from a shell loading plant explosion caused a large explosion in AN store, but the majority of the ammonium nitrate did not detonate.

March 1924 Nixon, New Jersey Nitration Works disaster – 17 fatalities – Q, C, S
A fire and several large explosions involving a vacuum graining vessel destroyed a warehouse containing ammonium nitrate. The explosiveness of the product was perhaps enhanced, as it had been prepared using nitric acid that had previously been used for the production of TNT.

August 1940, Miramas, France - S
240 tonnes of ammonium nitrate in sacks exploded after being hit by a shell from a nearby fire in a munitions train.

1966 USA - C
A fire involving AN fertiliser and other combustibles lead to an explosion

1973 USA - C
A fire in an AN wooden store resulted in the explosion of a few tonnes of AN.
14,000 tonnes were unaffected.

1978 USA - Q
500 tonnes of AN involved in a warehouse fire – no explosion

1982 UK - C
Major fire with wooden furniture stored near AN fertiliser.
Resulted in a deflagration and toxic fume release. Local evacuation undertaken.

1998 Kentucky, USA – Q
A warehouse containing 4000 tonnes of AN in basement was allowed to burn out.
Two explosions reported from propane cylinders stored there. Mass evacuation took place.

November 1988, Kansas City Missouri, USA – 6 fatalities – Q, D

Two trailers containing approximately 23,000 kg of ammonium nitrate exploded at a construction site. The explosives were to be used in the blasting of rock while constructing Highway 71. The responding companies were warned that there were explosives on-site; however, they were unaware that the trailers were essentially magazines filled with explosives. At 4:07 am one of the "magazines" caught fire and a catastrophic explosion occurred, killing all six firemen instantly — only sparing remains were found. A second blast occurred 40 minutes later, although all fire crews had been pulled back at this time. The blasts created two craters, each approximately 100 feet (30 m) wide and 2.4 m deep. The explosions also shattered windows within a 16 km area and could be heard 64 km away. It was later determined that the explosions were acts of u, set by individuals embroiled in a labour dispute with the construction company contracted to build the highway

September 21st, 2001 AZF Fertilizer Toulouse France 31 fatalities – C

The explosion had occurred in a warehouse in which granular ammonium nitrate was stored flat, separated by partitions. The amount is said to be between 200 to 300 tonnes of ammonium nitrate, which is used to make fertilisers. A spokesman for the Interior Ministry in Paris ruled out a criminal attack, saying the explosion had been caused by an accident following an "incident in the handling of products". The exact cause remains unknown in public domain with suggestions that the material was off-specification and contaminated (sodium dichlorocyanurate) rendering the inventory more unstable.

April 2013, West, Texas, USA – 15 fatalities – Q, ?

A fertilizer company caught fire. Around 20 minutes later, ammonium nitrate stored there exploded, levelling roughly 80 homes and a middle school. 133 residents of a nearby nursing home were trapped in the ruins. In all, 15 were killed, and about 200 injured. There were reports that the facility had stored more ammonium nitrate than it was allowed to, without regulation by the Department of Homeland Security.