Storage of Technical (Porous) Ammonium Nitrate

Erik C. Nygaard
Yara International ASA, Porsgrunn, Norway

Abstract

During the last years, ammonium nitrate has been involved in several accidents worldwide. This have caused increased focus on security and safety issues and resulted in:

- Revised Yara standards
- Revised international standards for storage and transportation
- Stricter regulations from national authorities in many countries.

During our work to verify our internal standards for porous ammonium nitrate (TAN) we found that the information available was confusing and non-conclusive. In many studies the TAN used had not been properly defined and therefore the interpretation of the results were difficult.
The main aim of this study was to verify safety aspects and to optimise the storage layout for porous TAN at our production sites. More specifically, the objectives were:

- To determine guidelines for the separation distances between stacks of big bags and between silos.
- To calculate the maximum storage amount based on the maximum allowable overpressure for facilities, storages and silos.
- Risk assessment of of TAN storage at our production sites

Tube tests where used to measure the blast waves from detonation of TAN and data from these tests were used to calculate the TNT equivalence. For TAN this was fond to be around 0.2.

Gap tests were performed to determine the critical gap length between an ANFO donor and the TAN (acceptor). The results of the gap tests were used in simulations to determine the critical separation distance between stacks of big bags and between storage silos. It was found that for TAN, the density as well as the stack configuration influenced the stack separation distance. For the TAN Grades tested, the "safe" stack separation distance varied between 7 m (23 ft) and 16 m (52 ft)

Layer of Protection Analysis (LOPA) of TAN storages at our production sites combined with the results obtained from detonation tests and simulations resulted in a completely new storage layout. In the past the general stack size had been 300 metric tons (330 short tons) and with a separation distance of 1 m (3.3 ft). This is now replaced by variable stack size dependant upon the distance to critical installations (roads, residential areas, ammonia tanks) and with stack separation distance of 7-9 m (23 to 30 ft).

Introduction

Ammonium nitrate (AN) is chemically speaking a simple salt with complex hazardous properties. The specific hazardous properties are determined by physical properties of the material (particle size, porosity and density), chemical properties (purity, stabilisers and moisture), environmental factors (confinement and compatibility with other materials) and conditions such as temperature and pressure. Generally speaking, the risk associated with ammonium nitrate in production, transport and storage is low.

Under severe conditions, all types of AN are able to detonate. Despite the low probability for the occurrence of a detonation under practical (including accidental) conditions, the hazards with AN should be understood due to the severe effects of such an event. The detonation properties (initiation sensitivity, detonation velocity and effect) of AN depend on many factors. With respect to safety in storage and transport however, the "sensitivity" of the material towards initiation is the most important parameter in controlling the hazards.

The "sensitivity" of AN is determined by the critical diameter (a detonation cannot be sustained below the critical diameter) and the response to thermal and shock stimuli. From both own experience and literature data, it appears that one of the main factors affecting the detonability of AN (critical diameter and minimum booster) is bulk density. From a study performed by Bauer et al. (1982) in the 70's it can be concluded that the critical diameter of high density AN (0.9 kg/l, 56.2 lbs/cu.ft) is in the order of meters.

In a recent study by TNO (Kersten) for the European Fertilizer Manufacturer Association that was presented at IFA Technical Symposium in 2006 at the it was found that critical diameter as well as critical initiation pressure for fertilizer grade AN was significantly higher than for TAN.

During our work to verify our own internal standards for porous ammonium nitrate (TAN) we found that the information available from other studies was both confusing and non-conclusive. In many studies the TAN used had not been properly defined and therefore the interpretation of the results were difficult.

Tests and results

A more detailed description of the tests and results of the tube tests, GAP tests and simulations can be found in proceeding from the 4th EFFE World conference on Explosives and Blasting in Vienna, September 2007.

In all tests performed, three types of TAN were used (Table 1).

	Bulk density (1 *l* cylinder) kg/l (lbs/cu.ft)	Oil absorption (%)	Average loading density, tube test kg/l (lbs/cu.ft)	Average loading density, GAP test (kg/l) (lbs/cu.ft)
TAN 1	0.81 (51)	7.6	0.84 (53)	0.83 (52)
TAN 2	0.72 (45)	12.1	0.72 (45)	0.73 (46)
TAN 3	0.79 (49.7)	10.7	0.81 (51)	0.80 (50)

Table 1: Characteristics of TAN samples tested

Tube tests: Determination of TNT equivalence

The main purpose of the tube tests was to determine the TNT equivalence of the test materials. The tests were performed at a test site in Älvdalen, Sweden, in close cooperation with FOI (Swedish Defence Research Agency). The tubes had diameter of 116 cm (46 inches) and a length of 400 cm (157 inches) and contained up to 4000 kg of AN (8 800 lbs).

The peak pressure plots was more or less equal for both directions (South and West). The TNT equivalence was also more or less equal for the three materials investigated and the fluctuations were small. The values of the TNT equivalences were more or less in agreement with theoretical values, based on energy release. The results showed that the TNT equivalence decreased with an increasing distance from the detonation. For one of the samples the TNT equivalence was found to be 0.60 at a distance of 40 m (131 ft) and 0.39 at a distance of 160 m (525 ft). The TNT equivalences in the present study were relatively high compared to values calculated from incidents (10 – 20 % TNT equivalence). In the interpretation of the equivalence values obtained in these tests it must be kept in mind that the tests were fully optimised with respect to configuration and very strong initiation source was used.

GAP tests

The purpose of gap tests was to determine the sensitivity of the materials (initiation pressure). In these tests the critical separation distance between a donor and an acceptor was determined, i.e., the minimum distance at which a sympathetic detonation between donor and acceptor is no longer possible. Same type of tubes was used as in the tube test, but length was about 200 cm (79 inches). The test showed that the critical separation distances varied between 2.0 and 3.0 m (79 and 118 inches), depending on which TAN grade that was used.

Simulations

In the gap test the critical separation distance between an ANFO donor and a TAN acceptor was determined. From the results of the gap tests the critical initiation pressure of the three TAN grades and the critical separation distances were determined with simulations. Note that in the gap tests ANFO is used as donor and TAN acts as the acceptor, while in the practical situation TAN is the donor and the acceptor. A detonation of TAN gives another pressure than the detonation of ANFO and therefore the critical separation distance in the practical situation is different from the gap tests.

Critical initiation pressure

In gap tests the critical separation distance between an ANFO donor and a TAN acceptor was determined. This was used to calculate critical initiation pressure for the three grades of TAN that was tested. To determine the critical initiation pressure simulations were performed with the computer programme Autodyn.

Separation distances and maximum storage amount

In literature, several tables with separation distances for AN can be found. Most of these tables seem to originate from the Table of Separation Distances (TSD) that was issued by IME in USA in the 70's. However, as described in notes to this table, ammonium nitrate, by itself, is not considered to be a donor when applying this table. Ammonium nitrate is only considered as an acceptor. If stores of ammonium nitrate are located within the sympathetic detonation distance of explosives or blasting agents, one-half the mass of the ammonium nitrate is to be included in the mass of the donor.

To overcome the disadvantages of the ATD and the pyrotechnical equation, a new approach towards the problem of critical separation distances was developed at TNO. The critical separation distance strongly depends on the initiation sensitivity of the AN. The approach above applies to material as produced. It is important to note, however, that the required separation distance significantly increases if the material becomes sensitised (for example by moisture, temperature or aging). This does not have to be a bulk effect; formation of a sensitised layer of material on the outside of a pile or stack might already be sufficient to affect the separation distance. Whether or not this effect has to be taken into account depends on many factors and on the scenarios that are taken into account.

Critical separation distances

On basis of the value of critical initiation pressure, simulations were performed to determine critical separation distances between stacks of big bags filled with TAN. The simulations were performed for a stack with three layers of big bags. From a previous study it was concluded that the way of initiation of the donor stack affects the critical separation distance between stacks. Therefore simulations were performed in which three different initiation points were used (See Figure 1):

1. Point initiation at the bottom of the bottom layer
2. Surface initiation at the bottom layer (height of 1 big bag)
3. Point initiation at the top of the middle layer

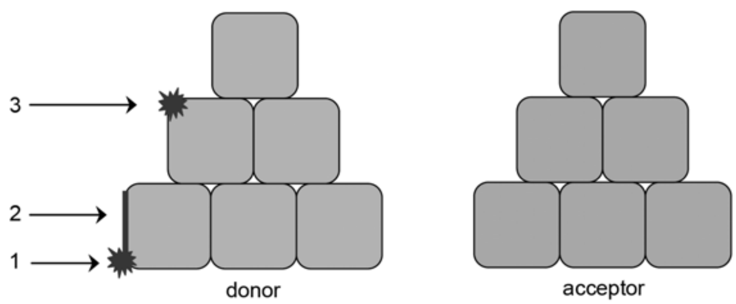

Figure 1: Initiation points for simulation

With “normal” layout of the stacks as shown above, the simulations gave a stack separation of 16 m (52 ft) for TAN with bulk density of 0.72 kg/l (45 lbs/cu.ft). For other samples tested, the stack separation distances varied between 9 m (29.5 ft) and 16 m (52.5 ft). By using a different stack layout (see Figure 2), the distances were reduced to 7-9 m (23 to 30 ft). (More details on these simulations can be found in my paper presented the EFEE conference in 2007, see reference list below)

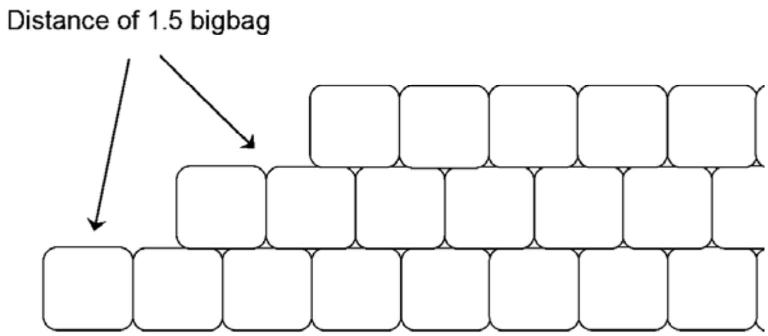

Figure 2: Modified stack configuration

LOPA Study (Layer of Protection Analysis)

The main objective of this study was to evaluate the storage layout for TAN at the Yara site in Köping, Sweden. The study involved all types of incidents that could have a negative impact outside the site, but in this paper I will only focus on the LOPA study for the warehouses for TAN storage.

Layer of Protection Analysis is a semi-quantitative tool for analyzing and assessing risk. It was developed in the late 1980's and most of the time it is used in the chemical industry. Although LOPA can be used at any stage in the life cycle of a process, it's most frequent use is during the design stage or when modifications to an existing process or its control or safety systems are made. LOPA is a simplified form of risk assessment as typically 'order of magnitude' categories for initiating event frequencies; consequence severity and the likelihood of failure of independent protection layers (IPLs) are taken into account. The method falls in between qualitative methods like HAZOP (HAZard and OPerability analysis) and What-if and quantitative methods like QRA (Quantitative Risk Analysis)

In LOPA one single scenario is taken into account. A scenario consists of a single 'cause → consequence' chain. The various parts of the chain are defined in the following paragraphs.

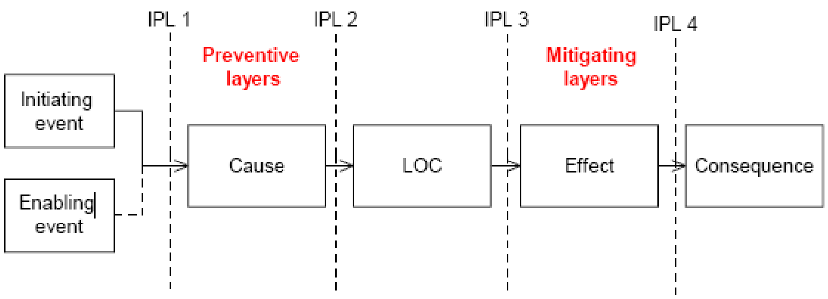

Figure 3: LOPA Scenario

Initiating event

The Initiating Event (IE) is the event that results in the accident scenario, i.e. it starts the chain of events leading to the undesired consequence. The frequency is '/year'. For the TAN plant we defined the following initiating events: shown in Table 2. It is important to bear in mind that LOPA is not a quantitative method, but uses an order of magnitude approach. Since an order of magnitude is used, it is easier to make estimation about incidents that are not exactly known. By using this method we can still say something about the safety of these incidents. We do not exactly know the frequency of the initiating event of a detonation of TAN, but we can estimate the order of magnitude. Tests by Kersten at TNO showed that the critical diameter for fertilizer grade AN is more than one meter (3.3 ft) and for TAN 15-20 cm (6-8 inches). TNO tests also showed that TAN had a critical initiation pressure of about 0.20 GPa (2kbar, 29 000 psi) while fertilizer grade AN needed a pressure of more than 2 GPa (20 kbar, 290 000 psi) to achieve initiation. Therefore we have defined the initiating event frequency for fertilizer grade AN to 10^{-6} and for TAN to 10^{-5} by this order of magnitude approach. The difference of these numbers is just 1 when calculating the Safety Gap (-Log). It can always be discussed how big the difference between these products are, but the impact on the calculated safety gap is not very significant. Making the difference in initiating event frequency smaller would only reduce it to a number between 0 and 1 in the safety Gap calculation. This is one of the advantages of the LOPA method. This approximation of event frequency may not be applicable to other risk assessment methodologies

Initiating event	Description	Frequency [/yr]
Fire	Without contaminant, electrical cabinets outside storage, no handling, no loaders left in storage	10^{-4}/yr
Fire	With contaminant, electricity or handling etc.	10^{-3}/yr
Detonation	Off-spec or uncontrolled material; contaminations	10^{-4}/yr
Detonation	Technical grade ammonium nitrate	10^{-5}/yr
Detonation	Fertilizer grade ammonium nitrate	10^{-6}/yr
Terrorism		N/A

Table 2: Initiating events

Likelihood	-Log frequency [/yr]
Well probable	<0
Occasional	0 – 1
Unlikely	1 – 2
Remote	2 – 3
Improbable/very unlikely	3 – 4
Nearly impossible/extremely unlikely	4 – 5

Table 3: Likelihood estimation

Enabling Event (EE)

An Enabling Event (EE) or Enabling Condition (EC) is a condition that is required for the initiating event to unleash a scenario and is expressed as probabilities. Examples of enabling events are start-up phase, material present, ignition source present etc. The enabling conditions and the conditional modifiers in the scenarios at Yara, Köping are determined for each scenario individually.

Cause

The cause in a scenario is the condition or state resulting from the event(s) that allowed the accident to occur.

LOC

The Loss of Containment (LOC) is the undesired event that one aims to prevent from occurring and is the point where the cause and consequence come together. Examples of LOC are spill of material, explosion, melting of (electrical) insulation.

Effects

The effects of an accident scenario are e.g. blast, dispersion of toxic materials, heat radiation etc.
The consequence is defined as the (undesired) outcome of an accident scenario. Consequences are expressed in terms of material damage, environmental pollution, injuries, fatalities or financial losses.

Consequences

The consequences are defined in a consequence table. In a risk matrix the acceptable frequency of the scenario is defined, which is called the LOPA Target Factor (LTF). The difference between the frequency of the scenario itself and the acceptable frequency (the LOPA Target Factor) is the Safety Gap (SG), which can either positive or negative.

LOC	Maximum Consequence class	LTF
Small fire	1	10^{-1}
Big fire	3	10^{-4}
Decomposition	3	10^{-4}
Fire to explosion	5	10^{-6}
Explosion	5	10^{-6}
Detonation	5	10^{-6}

Table 4: Consequence classes for the various LOCs.

Frequency of consequency [/yr]	Consequence category					
	Category 1	Category 2	Category 3	Category 4	Category 5	Category 6
$10^{0} – 10^{-1}$						
$10^{-1} – 10^{-2}$						
$10^{-2} – 10^{-3}$				Unacceptable		
$10^{-3} – 10^{-4}$						
$10^{-4} – 10^{-5}$		acceptable				
$10^{-5} – 10^{-6}$						
$10^{-6} – 10^{-7}$						

Figure 4: Risk matrix.

IPL

Independent Protection Layer (IPL) is a device, system or action that is capable of preventing a scenario from proceeding to the undesired consequence. There are two types of protection layers: Preventive layers, which can prevent the accident from occurring, and mitigating layers, which reduce the effect.

Layer#	Description	Purpose
1	Lay-out of the storage of ammonium nitrate	Minimizing domino effect, risk of rupture of ammonia tank and damage to village and road
2	Operator supervision	Early detection of abnormalities (e.g. fire)
3	Critical alarms and human interventions, Fire detection systems, sprinkler systems, interlock for conveyer belt	Detection of abnormalities (e.g. fire)
4	Post release physical protection (walls, dikes)	Reduction of consequences of incident, only at large ammonia storage tank
5	Plant emergency response	Protection of plant personal
6	Community emergency response	Protection of community

Table 5: Type of layers for protection for AN storage.

To prevent the occurrence of a scenario (or the consequences of an initiating event) only one layer of protection is required. The essence of LOPA is based on the fact that both preventive and mitigating measures have a probability of failure on demand (PFD). The primary purpose of LOPA is to determine if there are sufficient layers of protection against the scenario to balance the safety measures with the required safety levels. If insufficient safety measures are present, additional layers may be added. Or, the other way around, if too many layers are present, layers may be deleted (safety critical equipment or instrumentation). For a scenario to occur, all IPLs should fail.

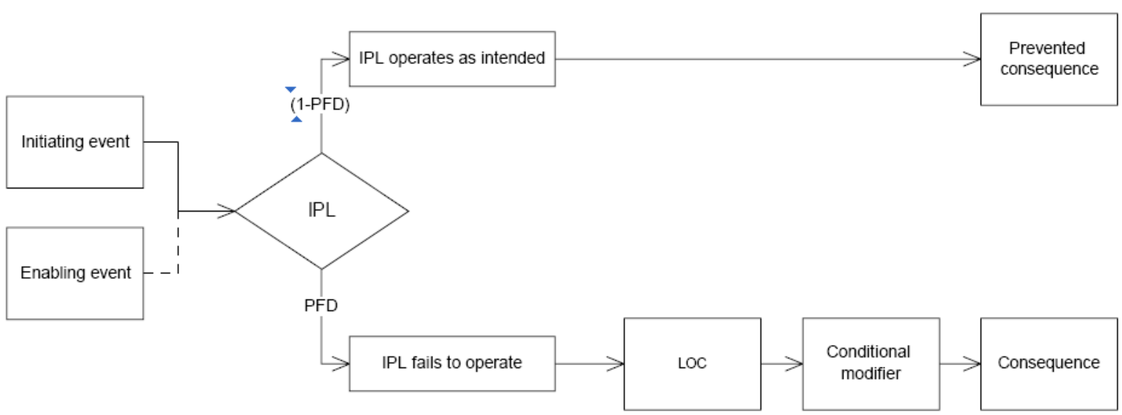

Figure 5: Components and structure of a LOPA scenario.

Warehouses in TAN Plant in Köping

In Scandinavia a probabilistic approach is normally accepted in risk assessment. However, our internal requirements states that severe damage to ammonia tank was to be treated in a strictly deterministic way, thus detonation in a stack should not give overpressure above critical level at this tank (= Category 6 in Figure 4). The old permits for storage at this plant specified a stack size of 300 metric (330 short tons) tons and a 1 m (3.3 ft) separation gap. With the internal requirement for risk assessment regarding damage to ammonia tank, it was found that max acceptable stack size (TNT equivalence of 0.20) for some of the existing warehouses would be very small and these warehouses had to be moved.

To evaluate each individual warehouse we identified a range of possible generic scenarios for fire, decomposition and explosion and performed a LOPA analysis for these scenarios.

1. Estimate the consequence and severity of a scenario for screening.
2. Select an accident scenario (single cause-consequence pair).
3. Identify the initiating event of the scenario and determine its frequency.
4. Identify enabling event or conditions (probability).
5. Identify outcome modifiers and their probability. Outcome modifiers are for example probability of ignition, probability of personnel in affected area or probability of fatal injury.
6. Determine the frequency of the unmitigated consequence (3*4*5).
7. Identify the IPLs and estimate the PFD of each IPL.
8. Estimate the risk of the scenario by mathematically combining the consequence, initiating event and IPL data.
9. Evaluate the risk to reach a decision concerning the scenario. In this step, the risk of a scenario is compared with the tolerable risk criteria or related targets (company dependent or determined by legislation).
10. Decide how much additional risk reduction may be required to reach a tolerable risk level.

Example: M13

M13 is used as storage tent for TAN in big bags, with a maximum amount of 5500 metric tons (6061 short tons) (2 months a year). The regular amount of TAN is fluctuating between 2000 and 3000 metric tons (2204 and 3306 short tons). At present the big bags are stored in piles of 300 metric tons (330 short tons) of three layers high with 1 m (3.3 ft) separation distance between the piles and between the piles and the wall.

General remarks about this storage are.

- The probability for contaminants in the big bags, e.g. too much coating, chlorine, metals and acid, is very low.
- No combustible materials and electric machinery are present inside the building.
- All lighting is approved and the light is outside of reach for trucks.
- Electrical distribution takes place outside the storage.
- Forklifts/payloaders do loading and unloading of the storage, and these are never parked inside the building.
- The storage has no connection to other processes. The distance to the nearest storage equals 18 m, so no sympathetic detonation can occur.
- The storage tent has no fire detection system.
- Outside the storage on the northeast side, 50 metric tons (55 short tons) of AN in bags on pallets are stored a few days a week. The probability for a large fire increases because of the presence of the pallets.

There is car/truck traffic outside the storage and this can be an extra source for an accident and a fire to occur. In this case the frequency of the initial event fire (without contaminants) changes from 10^{-4}/yr (see Table 2) to 10^{-3}/yr. The probability for a fire turning into an explosion is very low, because of the presence of people who can detect the local fire at an early stage.

On the northeast side of this storage a railway is situated with up to 16 railway cars each with a capacity of 30 metric tons (33 short tons) of TAN in BigBags. The minimum separation distance between these cars and M13 is 12 m (39 ft) for the first car. The railway cars are made of steel and have a wooden floor. Spreading of fire to all cars will hardly occur and not all cars will burn at the same time. The railway also contains railcars with 40 metric tons (44 short tons) of ammonia (8 bar) for 2 days a week.

Payloaders and trucks are driving around M13. Due to accidents between the payloaders and trucks, fire may occur. The combination of ammonium nitrate, fuel and a prolonged fire exposure can increase the chance for an explosion to occur. However, loading of the trucks occurs only during daytime up to 23.00 h. In case of an accident with fire, it is expected that the fire will be detected and the fire brigade will be on site within 5 minutes. A contribution to the fire scenarios is substantial, but because of the low probability of initiation this will not be a contribution to the generic mass detonation scenarios. The frequency for a traffic accident to occur is determined at 10^{-2}/yr. The probability of a detonation of the material outside the storage due to a traffic accident is smaller than 10^{-3}/yr. The probability of detonation inside M13 due to a traffic accident is the same as in Table 2 (10^{-5}/yr).

For a few days a week 50 metric tons (55 short tons) AN on pallets and in containers are stored around and close to M13. The pallets are loaded on rail cars. Due to the pallet material a small fire can easily spread and become a large fire and therefore the frequency of a large fire increases. Fire at the AN on pallets is worse than for big bags, because of the chimney effect with the use of pallets.

M13 – Big fire				
	Probability	Frequency [1/yr]	-Log	Remarks
LOPA target factor		10^{-4}	4	Consequence class 3
Initiating event		10^{-4}	4	
Enabling event	10^{-3}		3	Probability for amount of contaminants to cause big fire
IPL				
Conditional modifier				
Scenario frequency			7	
Safety gap			-3	
Risk tolerance criteria			Ok	

Table 6: Example: Result of LOPA Study, M13; Big Fire

One of the results of the LOPA study for the generic scenarios of M13 is shown above. For all scenarios it was found that the frequency of uncontrolled fire is 10^{-4}/yr based on the building characteristics. The frequency of detonation is 10^{-5}/yr, because M13 contains on-spec material.

The scenario of fire turning into an explosion is covered by the generic mass detonation. Taking the dimensions and amount of combustible material into account this gives a low probability for this scenario. The effect is further reduced by fire repression.

The containers close to M13 should stay at a minimum distance of 12 meters (39 ft) from the storage building (this is the same as the distance between the railcars and the building) to decrease the risk of a domino effect in case of detonation of the containers.

The chance for fire of TAN stored on pallets outside M13 increases from 10^{-4}/yr to 10^{-3}/yr due to the traffic (crane for unloading, railcar) around M13. The pallets are less protected against traffic accidents than the bags inside the building.

In addition, calculations showed that the max stack size for M13 is 190 metric tons (209 sh tons) with a separation distance of 7-9 m (23-30 ft) if revised stack configuration is used.

Conclusions

In the first part of this study the storage layout for porous ammonium nitrate (TAN) has been determined for three different grades.

- The TNT equivalence is dependent on the distance. In the interpretation of the equivalence value it must be kept in mind that these tests were fully optimised to produce a maximum effect with respect to configuration, and a very strong initiation source was used.
- In addition to the non-ideal effect in practical situations, the blast effects in the tests concluded that ammonium nitrate (TAN) does not possess the same effect behaviour as TNT. At short distances TAN gives a higher over-pressure effect, while the effect is smaller at larger distances. The TNT equivalences in the present work were determined at relatively short distances.
- The TNT equivalence, used for practical situations, is a combination of 'explosive power' and 'efficiency' (i.e., the part of the bulk which contributes to the blast effect in a detonation). The 'explosive power' is based on the TNT equivalence obtained in the tests. From a combination of the results of these tests, results of previously performed tests and the TNT equivalence determined in AN accidents, a TNT equivalence of about 20 % appears appropriate for practical situations. The value depends on the configuration of the stack, density and type of the material and the way of initiation.
- With this value for the TNT equivalence the maximum allowable amount of TAN in one pile or stack can be determined, based on the maximum allowable overpressures in the surroundings (e.g. storage tanks, road).

From the results of the gap tests the critical initiation pressures was determined for the TAN grades tested.

Simulations were performed to determine the critical separation distances between stacks of big bags to prevent sympathetic detonations between the stacks. Contrary to dense, fertilizer grade AN, the critical separation distance for TAN depends on configuration of stacks, way of initiation and density and type of material. By altering stack shape the critical separation distances were found to be 7-9m (23-30 ft) for the TAN samples tested.

It is very important to note that our tests were performed with TAN of high quality that had been stored properly. Any AN that is subjected to thermal cycling or absorption of water might dramatically change its properties and thereby become more sensitive.

Using the data for TNT equivalence and gap results we redesigned our storages. Some had to be moved to maintain stacks of acceptable size.

Finally, by using these results and LOPA method for risk assessment we had to redesign storages and install new "safety features" (smoke detectors, flame retardant belts, sprinkler systems etc.)

Acknowledgements

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