# HIGH CHALLENGE WAREHOUSING : AMMONIUM NITRATE AS A TYPICAL CASE STUDY

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(extended abstract - Sup-Det 2010 Symposium, 16 – 19 February 2010, Orlando, FL USA)

## 1 INTRODUCTION

Ammonium nitrate is a world-wide commercially important product. Two main industrial uses are essential regarding this chemical: one as a fertilization nutrient, the other as an explosive ingredient (e.g. for manufacturing ANFO). Full life cycle of those products require special attention for safety (and also security) management, taking account of the complex properties and specific hazard profile of the material[1]. The hazard profile of ammonium nitrate and related compounds depends on many parameters (like melting point, density, particle size spectrum, open and closed porosity, humidity, content in combustible matter, crystallographic structure…). Although industry has accumulated more than a century of experience on the manufacturing of ammonium nitrate and significantly improved intrinsic safety of the product, significant accidents (fires, explosions) still occur regularly, both in storage and transport, that justify appropriate attention from the regulators and all interested parties. As a result, ammonium nitrate storage is generally controlled by dedicated regulations and codes of practices and not treated as a simple oxidizer storage (as an example, in the USA, NFPA 490 deals with non explosive grades of ammonium nitrate based products where NFPA 430 addresses "generic oxidizers"; in the EU, the so-called '*Seveso* Directive' implementing risk management schemes four major hazardous industrial facilities has currently for entries for ammonium nitrate). The Toulouse accident[2], although not fire related, has boosted a general updating of many regulatory texts and codes of practice worldwide, but very few attention has been brought to detection and suppression of fires in such premises. Beyond essential prevention fire and explosion safety measures, like for instance avoiding the use of combustible materials in infrastructures of warehouses or isolating ammonium nitrate piles from incompatible materials, detection and suppression measures also play a crucial role for safe storage of in ammonium and ammonium nitrate based fertilizers, but defining adequate equipment and procedures still reveals challenging.. Examining more in details the safety profile from the main properties of the chemical and from lessons learnt from accidents is essential to define appropriate equipment and detection and suppression strategies.

## 2 BASIC SAFETY PROFILE OF AMMONIUM NITRATE

Early disasters (in the pre 1960 period) have justified significant efforts to qualify the safety profile of such a complex material that allow progressively more safe ammonium grades and ammonium based fertilizers be placed on the market.


**Figure 1 : visible smoke threat from ternary type NPK decomposition (Sweden, July 2004)**

Ammonium nitrate is stable at ambient temperature and pressure. In relation with the fire risk, it is important to notice the following information:

- the product itself doesn't burn but as an oxidizer, it support and enhance combustion of combustible matter ;

- the product melts at quite low temperature (170°C) at which complex decomposition process already starts even if significant decomposition rates require temperature levels of more than 200°C. . decomposition first develops endothermically and finally turns into exothermic reactions. Decomposition is liable to release significant amounts of atypical toxic smoke (see figure 1), containing ammonia and nitrogen oxides. In extreme conditions, not completely rules out, explosive reactions may be triggered (provoked thermally or mechanically)
- numerous incompatibilities have been identified with ammonium nitrate, that may significantly increase the fire and explosion risk at both manufacturing and storage and lower the decomposition onset temperature in many cases.

According to known properties, hazardous scenarios with solid (prills, granules) ammonium nitrate and ammonium nitrate based products may be classified in three main categories, mostly in relation with the fire hazard (as an initiating event) and the type of accidental scenario that has to be considered:

a) *detonation* : although of very low probability of occurrence, the risk pertains to all technical grades of ammonium nitrate, straight and possibly compound fertilizers containing significant amounts of ammonium nitrate (no true threshold in terms of AN content can be quoted, as it depends on manufacturing process, other ingredients in the mixtures, etc ; molten phases of ammonium nitrate may be very sensitive to detonation[3]

b) *simple decomposition* process relating to heat stress provoked e.g. by an external fire (such as illustrate in figure 1) ;

c) special "*cigar burning*" accidental behavior involving some qualities of NPK type fertilizers: such incidents have been experienced in fertilizers warehouses and .in maritime transport cargoes. This peculiar phenomenon is also referred to as *self sustained decomposition* (SSD).

## 3 WHAT DO RECENT ACCIDENTS TEACH US

Numerous careful reviews of past accidents involving ammonium nitrate based products were done in the past[4]. Very old disasters were linked to massive detonation scenarios (Oppau, 1921, Germany, detonation of AN+AS, 509 fatalities, Texas city, 1947, USA (explosion of wax coated AN following a fire in 2 ships, > 600 fatalities); Whether not related to a fire event, The Toulouse accident (21st of September 2001) essentially revealed to all stakeholders the need to take special care of 'off-spec' products, by nature presenting not well defined hazardous properties. Smoke and heat venting is highly challenging inside storage buildings. Fertilizer 'fire' intrinsic plumes present much lower buoyancy that conventional fire plumes, leading to specific overall thermo-physical behavior. Temperatures are also much lower than in conventional fires. In many cases early detection is not achieved, rendering fire fighting operations inside the building ineffective or impossible. Indeed, first emergency response inside the premises requires special personal protection like breathing apparatuses and the use of fixed fire hose reels will often reveal not manageable. However, large amounts of water are the only way to extract heat for mitigating AN decomposition processes. Recent accidents also revealed the importance that molten phases may play in a 'detonation following a fire scenario'.

## 4 ELEMENTS OF DETECTION AND SUPPRESSION STRATEGIES

Few existing regulations or codes of practice provide specific advice or requirements in the field of detection for facilities storing ammonium nitrate based products, probably reflecting the absence of dedicated research in the matter. In France the subject was recently discussed by the concerned industry and some consensus is reflected in table 1. In France, some research justified the use of nitrogen oxides emissions to detect ammonium nitrate 'fires'. The use of thermal imaging appears to be a new trend. Combination of at least two detection techniques is preferable. Corrosive ambiance in such warehouses must also be considered for both detection and suppression strategies on the long term, as well as potential for false alarms, as those sometimes induced by normal heat and smoke signals of handling vehicles or belt conveyors …).

Water is the unique media that is adequate to tackle fires involving ammonium nitrate decomposition, as confirmed by nearly all regulations and recommendations. Debate is still open however on the water requirements that would best fit fire fighting needs and cope with pollution issues. Indeed, large amounts of water seem preferable owing to physico-chemical properties of ammonium nitrate. Quasi-infinite water solubility of the product however trigger the requirement to contain fire waters due to ecotoxicity (common to many nitrates). Special attention must be paid to NPK type fertilizers capable of self sustained decomposition (SSD). Decomposition residues (half the weight of initial material) may form a water tight shell that need to be overcome by adequate self penetrating fire hose systems for efficient cooling operation.

**Table 1 : view points on different detection strategies as compiled by the French fertilizer industry (2008)**

(Notice : a), b) and c) refer to same notations in section 2)

| *Detection principle* | *advantages* | *shortcomings* | *Expected scenarios* | |
|---|---|---|---|---|
| | | | *c)* | *a) & b)* |
| Temperature detection | Buying and maintenance costs may locate decomposition | Late detection (low heat conductivity) | + | - |
| Ionization detector | Fast response, inexpensive | Low sensitivity, false alarms | + | ++ |
| Aspiration smoke detection (optical) | Accuracy, reliability, fast response | Costs, maintenance | +++ | +++ |
| $NO_x$ detection | Suitable for all types of AN based products ; unit cost, ease of use | Overall cost according cells #; late detection, maintenance, signal noise | +++ | ++ |
| $N_2O$ detection | Suitable for all types of AN based products, early detection, reliability – | Cost, maintenance ; Aspiration network, clogging only appropriate for large areas | +++ | ++ |
| Infrared flame detection | Detection of flaming sources of ignition ; fast response | Non flaming fires or AN decomposition not detectable | - | ++ |
| IR cameras | Early detection of hot spots , image processing | Cost ; maintenance | +++ | +++ |
| Standard camera | Suitable for large warehouses | Requires human analysis ; cost – maintenance ; overlapping of storage areas requested ; night ? | ++ | ++ |

## 5 SUMMARY

Appropriate fire detection and suppression strategies are of prime importance to tackle fires in ammonium nitrate storages, beyond prevention measures. Quite specific phenomenology regarding 'fire related' decomposition of ammonium nitrate based products, in relation with type of AN products must be taken into account for appropriate detection and suppression implementation plans. It is important to stress that – by a single exception (the Toulouse case – no fire related)-, all significant recent accidents that actually ended by a detonation of ammonium nitrate started by a fire, where the development of molten phases of the product have likely played a crucial role in activating a detonation process. Indeed, all technical barriers against explosion brought at the manufacturing step in the granular form of the product are inhibited by melting. Experience seem to stress that time available for 'global intervention' (detection + suppression) in case of a significant fire inducing AN decomposition –if explosion do trigger at the end- is less than one hour. In case fire is not detected and put under control very quickly, evacuation of exposed population to toxic smoke fire threat and detonation risk remains the only alternative in extreme cases, as in the case of the Bryan incident (TX, July 2009), notwithstanding decomposition without detonation keeps the more frequent issue in such a case.

## REFERENCES


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