

# Safety and security issues relating to low capacity storage of AN-based fertilizers

Guy Marlair\*, Marie-Astrid Kordek

*\*INERIS, Parc Technologique Alata, BP2, F 60550 Verneuil-en-Halatte, France*

Received 22 October 2004; received in revised form 9 March 2005; accepted 14 March 2005

Available online 10 May 2005

## Abstract

Motivated by both the Toulouse explosion, and a series of recent unexpected handling and storage accidents in well-developed countries, the safety issues associated with the storage of fertilizer grades of ammonium nitrate (AN) are considered with a focus on low storage capacity premises. Such facilities are numerous and, in large agricultural countries, include thousands of end-users and hundreds of small distributors. The strong oxidative (sometimes explosive) properties of products containing significant amounts of AN have led to a long history of major accidents including mass explosions in large storage units and pre 1950s, to mass explosions in ships. A major breakthrough in safety was achieved in the 1950s, with the promotion – amongst other improvements – of better anti-caking agents. Although modern AN fertilizers complying with current standards are not considered as explosive material per se, the latent risk of accidental detonation under specific conditions remains a real issue, and from a scientific point of view, cannot be completely ruled out—as dramatically demonstrated by the Toulouse disaster in France. The new insight provided here is derived from: (1) a literature review on hazardous properties of AN and AN-based fertilizers; (2) a review of accidents focusing more particularly on the reporting of recent new cases involving relatively small quantities of previously ‘thought safe’ products; (3) an examination of both the relevant regulatory framework and the level of hazard control achieved; (4) appropriate discussions of the economical, technical and organizational factors that could lead to some underestimation of the risk compared to large scale storage facilities.

In terms of research requirements, the complex potential scenario ‘mass explosion following a fire’ requires further attention, as does the role and properties of molten ammonium nitrate, which could be the precursor for such an event to occur. Beyond research needs, reinforced legislative control by the authorities and further promotion of safe storage practices must be encouraged by the industry for end-users particularly. Such users have inherently the highest potential for undesirable situations, due both to the nature of their activities and also a possible lack of awareness of the real danger.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Ammonium nitrate; Fertilizers; Storage; Safety; Explosion

## 1. Introduction

Two commercially important grades of the chemical ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) are in use on a worldwide basis. One refers to the (porous) technical grade of the product as a key ingredient for blasting agents or high explosives: in this case, for industrial applications, the chemical is commonly mixed with fuel–oil, and then referred to as ammonium nitrate fuel–oil (ANFO). AN-based fertilizers are the

other most well-known trade outlet of the chemical for agriculture. For this latter purpose, the grade of ammonium nitrate in use differs only slightly in terms of physico-chemical properties compared to the technical grade (e.g. lower porosity, higher density, minor difference in particle size), but AN fertilizer grades are much more controlled in terms of detailed specifications requirements for commercial distribution. AN-based fertilizers in the widest sense refer to a variety of commercial products, roughly classified by the profession in two types [1]: (a) straight nitrogen fertilizers, where the element nitrogen is the principal plant nutrient (AN fertilizers, calcium ammonium nitrate (CAN) fertilizers, and ammonium

\* Corresponding author. Tel.: +33 3 4455 6370; fax: +33 3 4455 6510.  
E-mail address: guy.marlair@ineris.fr (G. Marlair).

sulfate/ammonium nitrate (ASN) mixtures); (b) compound (complex or blend) fertilizers: these are NPK/NP/NK products that contain, in addition to nitrogen (N), at least one other nutrient such as phosphate (P) or potash (K).

Accurate (legal) designations of AN-based fertilizers may differ according to the areas of production and use, in relation with local or regional specification standards and regulations in application. For instance, AN-based fertilizers as designated ‘EC fertilizers’ [2] now refer to limited and well-specified series of inorganic, essentially straight, N containing fertilizers (all listed in Annex I of the new EC regulation 2003/2003 relating to fertilizers [2], see no. 5, 6, and 8 product series in the list).

The present study focuses on storage safety and security issues relating to those products containing ‘significant’ quantities of ammonium nitrate (such as the products termed in France by the appellation ‘*ammonitrates*’ as still confirmed in the French official version of ref. [2]), classified most often as an oxidant material (class 5.1), according to United Nations recommendations on the transport of dangerous goods [3]. With those fertilizers, the hazard of explosion keeps a latent (although unlikely) threat in accidental circumstances. In the context of this paper, the products of interest are hereafter referred to as AN fertilizers, but are not necessarily restricted to those ‘straight’ fertilizers with high dosage in nitrogen from AN, as might erroneously be assumed, since some compound fertilizers may contain as much as 80% (or even more) of AN and shall therefore also deserve due safety consideration.

From an overall point of view, however, safety issues are more sensitive with straight AN-based fertilizers, according to state-of-the-art and current records of accidents involving nitrogen containing fertilizers.

The general context of the AN fertilizers storing issues has at first to be related to the tremendously large market existing for the use of the products, even in the brand new ‘sustainable agriculture’ promoted at the opening of the new century. The important marketing features worth to be pointed out are:

- (1) enormous amounts of products flows in all continents (some 40 million tons of products produced in 1999–2000, according to UNIFA<sup>1</sup>);
- (2) high variability in the distribution framework of products from one country to another;
- (3) hundreds of AN-based actual formulations;
- (4) complexity of the warehousing issues, due to high and seasonal variation in stocks, and due to technical, including storage capacity, economical et regulatory factors.

On the one hand, very large AN fertilizers stores liable to contain several thousand tons of products are rather limited in number and well identified, since registered by the authorities in charge of the control of major industrial hazards. These facilities are most often located within manufacturing plant boundaries or are dedicated large storage premises (see Fig. 1).



Fig. 1. View of a dedicated facility for AN-based fertilizer storage.

On the other hand, fairly numerous ‘small’ deposits exist and their characteristics generally depend on local rules or consumption habits. A general concern pertaining to these low capacity storage premises lies in the very limited control of potential risks for the operators and their neighbors. Examples of potentially significant threats with regard to AN fertilizer storage are arson (deliberate fire), quite frequently identified as cause of farm fires for instance [4] or terrorism making sometimes use of explosives obtained from robbery or derived from explosive ‘substitutes’.

This is the reason why the following issues have to be carefully examined: how safe and how secure are small storage areas of AN fertilizers compared to larger ones, due to inherent hazards of AN products, risk typology of small storage, and considering safety standards pertaining to these products, and control being provided by existing national or international regulatory framework?

## 2. Hazardous properties of AN-based products: a reminder

We essentially report in this section on important properties and hazard description and rating attributed to the chemical and related fertilizer products by technical literature.

### 2.1. Important properties and related hazards of pure ammonium nitrate and AN products

#### 2.1.1. Ammonium nitrate $NH_4NO_3$

**2.1.1.1. Physico-chemical properties.** As a pure chemical, the properties of  $NH_4NO_3$  have been extensively studied and are thus well referred to in many handbooks and datasheets. In solid physical state, ammonium nitrate is chemically stable at normal temperature and pressure. It has a melting point of 170 °C and begins to decompose at 210 °C (value supported by small-scale adiabatic test results). Adiabatic calorimetry tests involving large samples of some 100 g, reveal that

<sup>1</sup> French professional syndicate: Union des Industries de la Fertilisation.

Table 1  
Ability to detonation (or explosion), as expressed by some safety oriented documents

Source	Hazard identification and rating
NFPA 49 [5] NJ, USA [6] Weiss [7]	“If subjected to strong shocks or heated under confinement causing a pressure build-up, may undergo detonation” “Ammonium Nitrate is a highly reactive chemical and a dangerous explosion hazard” “Fire: may cause fire and explode on contact with combustible”
The Netherlands [8]	“Explosion: can explode if mixed with combustible substances” Footnote: “Becomes shock sensitive when contaminated with organic substances. In confined spaces combustion can cause explosion”
Pohanish and Greene [9]	A strong oxidizer. With reducing agents, combustibles, organic materials, finely divided metals may form explosive mixture or cause fire and explosions
Fire Service, Switzerland [10] UK [11]	(Refers to ‘solid ammonium nitrate’): does not burn but is explosive and oxidizing <sup>a</sup> “It may explode if heated to high temperature in a container. It explodes more readily if contaminated with combustible materials”

<sup>a</sup> Translated from the French wording: “Le produit ne brûle pas mais est explosif et comburant”.

AN decomposition may start even earlier (190 °C) [29]. The molecular weight is 80, of which the nitrogen element accounts for 35%. The relative density is close to 1.7; the bulk density is close to 0.9. The solubility in water quite high, about 190 g/100 ml at 20 °C. Chemically, the strong oxidizer property explains high reactivity potency with numerous “incompatible” chemicals, which behave as powerful catalyst agents in oxidizing reactions. This is therefore a key factor when analyzing safety issues regarding handling and storing AN industrial-related products, including AN fertilizers.

2.1.1.2. *Explosion hazards.* Table 1 gives an insight on AN major hazards in relation with the fire and explosion risks, as perceived, sometimes rated, by a variety of technical authors.

### 2.1.2. *Explosion hazard pertaining to fertilizers with high AN content*

AN-based fertilizer products have been similarly reviewed from technical literature sources in terms of reported hazards. The accurate wordings used to describe them are listed in Table 2.

Similarly to most industrial products, the properties of AN-based fertilizers may deviate from nominal composition

in active substance due to the presence of desired additives and impurities due to processing the AN fertilizers.

For authorized AN-based products, these deviations are generally highly controlled by legislative frameworks that are stipulating narrow tolerance figures around mentioned additive specification contents. Indeed, high nitrogen AN fertilizers will present chemical properties (including potency to explosive reaction) highly influenced by their carbon content, but they may also be influenced by other trace elements such as metals. Table 2 is a sample on how the detonation hazard pertaining to the fertilizer grade of ammonium nitrate is currently described.

It is recognized that high AN content fertilizers can detonate in specific conditions: these conditions are, however, not totally ruled out on a scientific point of view, despite of intensive research carried out in the past [12,14,15,28]. This leads to considerable variation in the wording used in technical literature to qualify the explosion hazard property of AN-based products. Tables 1 and 2 provide clear illustration of that latter statement.

However, a high nitrogen content in the product was identified years ago as a key factor (for sure only one of those!) in the detonation ability. This is the reason why most current

Table 2  
Ability to detonation of AN fertilizers, as stated by some fire-safety oriented useful documents

Literature source	Hazard identification and rating
Fire Protection Handbook, USA [12]	‘When (fertilizer grade) AN is intimately mixed with fuel-oil, ground polyethylene, or ground paper, transition from burning to detonation is possible, although quite unlikely, in piles sizes that are typical of those found in storage and transportation’
EFMA <sup>a</sup> guidance document [13] International Fertilizer Society (IFS) [35]	“It has high resistance to detonation. Heating under strong confinement can lead to explosive behavior” ‘AN is especially difficult to detonate [. . .]. Heating under confinement and shock initiation of hot or contaminated AN by projectile impact appear to be more credible mechanisms in the context of industrial operations. A number of factors can facilitate detonation or energetic deflagration taking place by these mechanisms, they include strongly acidic conditions, presence of bubbles, presence of contaminants, limited venting, presence of critical mass and prolonged heating
EFMA 2004 Guidance for sea transport of ammonium nitrate-based fertilizers [1]	AN-based fertilizers are capable of detonating under certain conditions, requiring a strong source of ignition. Standard good quality fertilizer products have high resistance to detonation [. . .]. This resistance, however, can be adversely be affected by a number of factors such as substantially smaller particle size, higher porosity [. . .] high levels of combustible, organic and other sensitizing materials [. . .]. Heating under severe confinement can also give rise to a potential explosion hazard

<sup>a</sup> European Fertilizers Manufacturers Association.

regulations and codes differentiate AN fertilizers categories according to AN content ranges. This leads to designation of low dosage AN and high dosage in AN fertilizers, based on their AN content (or equivalent nitrogen content) threshold values. In practice, the triggering threshold limit, however, differs according to countries. For instance, in latest EU regulation [2], high N content AN-based fertilizers are defined as those having more than 28% of nitrogen from AN (e.g. 80% of AN). In the NFPA 490 code [16], the threshold value requesting the application of the standard is only 60% of AN. In a more general way, safety requirements enforced by law regarding AN-based fertilizers are generally stipulated in due account of such low/high (sometimes medium) dosage in Ammonium nitrate, including, as an example, the requirement of a ‘detonation test’ for the ‘EC fertilizer’ marking. According to current knowledge, it appears quite difficult (if feasible) to define an absolute lower ‘safe’ limit in terms of AN content in a fertilizer grade that would definitely suppress any risk of detonation, whatever the other characteristics of the products are, as many parameters might play a role. As a result, values as low as 15.75% in nitrogen have been retained in several recent official documents (see Sections 4.1 and 6) as a safeguard value for inorganic AN-based fertilizers.

## 2.2. Conventional hazard ratings

### 2.2.1. Classification of the chemical and related AN fertilizers according to European Directives framework

Surprisingly, neither the chemical AN, nor the AN-based fertilizers are classified as a dangerous substance or a dangerous preparation so far according to concerned regulations (i.e. Directive 67/548/EEC [17] and 1999/45/EC [18], respectively), contrary to UN rules prevailing for the transportation of so-called ‘dangerous goods’ (see Section 2.2.2).

### 2.2.2. Classification according to UN recommendations for the transport of DGs [3]

AN-based products with high dosage in ammonium nitrate are classified as oxidizers in class 5.1 (see e.g. document [30] for more details on AN-based products classification schemes), although the testing procedure on which is based the classification, according to relevant UN recommendations for the classification of dangerous goods for transportation, is quite similar to the one in use for the mentioned European Directives regarding the classification and the labeling of dangerous substances and preparations. This is the result of ‘thought minor’ differences in the respective testing protocols that lead to the conventional rating of the oxidative hazard in the mentioned contexts.

Noteworthy to point out, within the coming Global Harmonized System [19] at the United Nations level (Waight [20] gives a global overview of potential implications of this new system firstly published in 2003), the previous situation will have to evolve to some common ‘compromising’ classification with straight high dosage AN products.

### 2.2.3. Classification according to NFPA 704 [21]

This classification scheme is intended to facilitate emergency response plans, in particular for fire services. It is also well known as the diamond code. According to the rules, classification of ammonium nitrate is given as follows [22]:

- health hazard rating (blue): 0 (at normal temperature, out of a scale from 0 to 4);
- flammability hazard rating (red): 0 (at normal temperature, out of a scale from 0 to 4);
- instability hazard rating: 3 (out of a scale of 0–4);
- designated hazardous property (lower white case in the so-called “diamond” code): ‘Ox’ (an additional rating for substances with readily oxidizing properties).

It is worth to mention that according to the NFPA 704 classification criteria, the ranking regarding the instability hazard is qualitatively described as “materials that in themselves are capable of detonation or explosive decomposition, but that require a strong initiating source or that must be heated under confinement before initiation”. According to that standard, the criteria is measurable in terms of an “instantaneous power density” parameter.

## 2.3. Fire and explosion hazards of AN products according to current knowledge

Numerous research as well as regular survey papers have been produced as regard the danger aspects of fertilizers containing ammonium nitrate, since the 1950s, by professional organizations as well as technical research centers (see for instance [12,14,15,23–25]).

To summarize very drastically, the hazards are threefold, due to the above-mentioned main properties of the chemical  $\text{NH}_4\text{NO}_3$ :

### 2.3.1. Fire related hazard

The product is clearly not combustible by itself (inorganic material), but is obviously able to sharply support a potential fire, as a carrier of in situ oxidizing agent ( $\text{O}_2$ ,  $\text{NO}$ ): it is therefore classified as an oxidizer. Accordingly, when thermally affected by a fire scenario involving slightly combustible to highly flammable products, the interaction of AN fertilizers will at least contribute to intensify the fire process.

### 2.3.2. Hazard related to thermal decomposition

When AN fertilizers are heated above some  $190^\circ\text{C}$  (in real life situations), decomposition of AN fertilizer occurs as an irreversible process, giving off toxic gases containing essentially  $\text{NO}_x$ . More information is available in terms of decomposition products and their distribution (remaining  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_3$ ,  $\text{NO}_x$ ,  $\text{N}_2$ , ...) versus temperature in refs. [25,26].

When fires do no longer effect AN fertilizers piles, the decomposition stops, as opposed to compound fertilizers, where self-sustaining decomposition could occur [27]

### 2.3.3. Explosion hazard

The explosion hazard with AN fertilizer is not intrinsically different from the explosive grade of the chemical, as largely proven by ‘intended’ misuse of AN fertilizers and other nitrate-based fertilizers by terrorists (e.g. first terrorist attack against the World Trade Center in New York City in 1993 [54], and Oklahoma City in 1995) and by accidental case histories, it is useful to recall, however, that the  $\text{NH}_4\text{NO}_3$  is not a so-called “sensitive” explosible material. A high activation energy is required for any mass explosion of AN fertilizer to occur. A fire scenario (other energy sources possible), however, presents such a high energy potential needed for possible consecutive explosion activation of AN fertilizers, depending on other environmental parameters. Confinement as well as contamination of the products (e.g. by organic material) constitute aggravating (commonly thought required) factors. Particle size distribution also plays a role.

## 3. Accidents: old and possibly new learning

### 3.1. Well-admitted lessons from major scenarios

It is well admitted from the past accidents that not only manufacturing those products, but also handling, storing and transporting them in massive quantities may be a source of safety concerns for people and the environment: several reviews of past accidents have been made available, including by the profession [31]. Both detonation hazard and self-sustained decomposition of AN-based fertilizers have been confirmed until recently at large scale accidental scenarios. The risk of self sustained decomposition (SSD) of NPK type compound fertilizers were at latest experienced in a storage facility when the Fertiberia plant accident took place in Murcia, Spain, close to the seaside, in January 2003 [32]. A characterization of that type of hazard [27] was undertaken years ago by INERIS in its fire gallery (motivated by the significant similar accident that took place years ago in a fertilizer warehouse in Nantes [33]) and further research on the matter is currently being done at a smaller scale. The Spanish accident confirmed that SSD was not a hazardous scenario strictly limited to ‘V shaped’ compound formulations.

The explosion hazard of AN fertilizers obviously reveals from past major accidents a bigger threat in terms of extent of immediate potential consequences. Indeed, a number of those tragedies, such as in Oppau (Germany, 1921), Texas City (USA, 1947) and Brest (France, 1947), have killed hundreds of people, injured many more and led to massive destruction. As a positive impact, considerable attention was paid by all stakeholders including manufacturers, professional associations, research centers and regulators, for the promotion and control of more reliable manufacturing processes, and inherently safer AN fertilizer products (no more wax coated high content AN fertilizer . . .). Better storage and handling practices in large warehouses were furthermore allowed, as a result. Reported by Shah [35], a first achievement was in-

deed a decrease in both apparent frequency and gravity of AN related accidents, since the 1950s. Quality driven standards, better anti-caking processes and regulation frameworks have clearly contributed to reduce the risks. Examples of such systems are the NFU 42.001 standard well known in France [34], equivalent in terms of product quality specifications of straight AN fertilizers to the European regulatory framework aiming at the designation of ‘EC fertilizers’. Other types of regulations are focused on the control and management of major industrial hazards (such as the *Seveso II* directive in Europe) and consequently most large AN fertilizers storage facilities are duly registered and submitted to strict safety requirements to prevent and mitigate accidents. However, the late tragedy of the AZF manufacturing plant in Toulouse in September 2001 [36,37] abruptly raised a ‘hidden’ concern regarding the safe storage of ammonium nitrate-based fertilizers in manufacturing plants. The community learnt that, as for many other chemicals and materials, AN-based fertilizers require due attention as regards to safety on the whole life cycle of the related products, including ‘out of spec.’ related compounds in loose storage. Records of major accidents are very often followed by appropriate improvement of related safety regulations and appropriate involvement of concerned industrial to render their products safer. This accident was the latest case of a series that led in the past to successive reviews of existing risk controlling tools on a worldwide basis, including by the standardization and regulating bodies. As a result, more stringent regulation frameworks and standards were progressively set up at both national and international levels that provide better control of large storage facilities where the potential consequences, in case of an accident are the largest. Due to extremely large amounts of AN consumed by the market at international levels, large storage capacity are existing in limited numbers on or nearby sites of production or AN blends manufacturers and to the key distributors. In details, the distribution sector of concerned products as well as the characteristics of the numerous end-users in the agriculture and gardening area leads to more variable situation in terms of AN storage size; therefore, justifying our analysis from a safety and a security point of view. As outlined by a few examples in the following section, low capacity stocks of ammonium nitrate, even meeting the more stringent quality standards available today, are presently unfortunately not exempt of any remaining explosion risk (see Section 3.2).

### 3.2. New lessons from a series of post 1970s case histories?

As explained in Section 3.1, the period 1950–2000 experienced much less fatalities from serious accidents with AN products compared to previous equivalent timeframe (some 20 fatalities compared to more than 1200), as reported by Heather [31]. This author was, however, too optimistic on his conclusions about post 1950s safety records. Indeed, all stakeholders have expected that the Toulouse accident was an exceptional event that would not actually compromise

Table 3  
A selection of recent accidents having involved limited amounts of AN fertilizers

Date, location	Activity/description	Product	Accident type/casualties	Time to explosion <sup>a</sup> (min)
1972, Taroon Australia [31]	Road transport: fire then explosion	Low density AN prills in bags	Three fatalities	45 [20]
1973, Cherokee, OK, USA [39]	Storage severe fire in AN store of wooden structure, fuel tank in pay-loader, difficulty with fire fighting	Fourteen thousand tons of AN fertilizers in the warehouse, but only a limited amount of it (<10 t) participated in the accidental scenario	A fire is the initial event A few tons only of the AN fertilizer stock exploded No injury	~50
1997, Brazil [31]	Road transport	Truck loaded with AN fertilizer trapped in a fire scenario caused by a nearby petrol tanker Quantity unknown	Delayed explosion, possibly initiated by an exploding propane bottle on the trailer	Unknown
2000, FL, USA [31]	Road transport. Collision between AN truck and gasoline tanker. Fire allowed to burn out	AN fertilizer, quantity unknown	Fire only	–
October 2003, Saint-Romain-en-Jarez, France [40]	End user storage	AN fertilizers (33.5) in bags (some 5 t)	Three heavily injured	~60
February 2004, Barracas, Spain [41]	Road transport: fire then explosion	Twenty-five tons AN fertilizers (33.5), bulk load (?)	Two fatalities, 3 people injured	~30
May 2004, some 50 km far from Bucharest, Romania [42]	Road transport: truck road accident then fire followed by explosion	Twenty-five tons (?) of AN fertilizers, in bags	At least 18 fatalities (including truck driver, firemen and policemen) and numerous injured people	~55

<sup>a</sup> Duration estimated from available information between fire event and explosion related phenomenon.

the global trend with AN fertilizers accidents. The coming half decade might, however, look statistically worst in the field due to the occurrence of a new series of accidents, some of them having involving limited quantities of straight AN-based fertilizers of high nitrogen content. The accidents we are referring to in our analysis are listed in Table 3 that also includes the well-known *Taroon* and *Cherokee* accidents, for reference. Readers will notice that we do not mention the middle and far-east 2004 transportation accidents (actual disasters indeed) that involved AN products in Iran and North Korea (since thought out of our paper scope) [38].

With the exception of one accident in Florida, where only a fire was observed, all listed accidents in Table 3 have led, as an ultimate event in the accidental scenario, to a mass detonation with significant consequences.

A fire event starting during a road transport involving AN products may be a major concern, as illustrated by the *Taroon* accident (1972) or by the accidents in Brazil (1997) or in Florida (2000). Such an event first results in a high thermal energy source impacting potentially some 20/30 t of products with a high and more or less rapid potential for contamination by organic materials, either due to presence of combustible materials (fuel, lubricating oil, tyres from carrying truck by itself), or from external cargoes after a crash.

Contamination is also potentially favored under those circumstances by the low melting point of ammonium nitrate. For many people, the event remains unlikely to lead to a detonation, except for low density AN grade, due to the absence of confinement. Supporting this view apparently, the Florida accident (2000), that was reported to experience a long lasting fire event did not affect significantly the AN-based fertilizers involved (no explosion), contrary to the *Taroon* scenario, where the “explosion following a fire scenario” might have to be attributed to the more sensitive technical grade transported.

However, the Cherokee accident was perhaps the first sign that the reality of the ‘explosion following a fire’ event occurrence with AN-based products is much more complex to analyze in terms of risk evaluation. A first statement is that very limited amount of ammonium nitrate took part of the explosion (5–10 t including the product in the conveyor and packed materials lying nearby), whereas the major heap of product (14000 t) remained unaffected by the explosion process [39]. Contamination by wood or oil material may have contributed to the accident and the pay-loader may have played a role in terms of confinement source. Noteworthy to say, the explosion is known to have taken place some 30–40 min after the initial fire event. However, an exploding propane reservoir may controversially have caused the detonation process [31]

Ultimately, the three last records of serious accidents in the list, with the last one having killed 18 people, all took place in Europe very recently and deserve careful attention. They at least show we still have gaps in our knowledge about safety issues with the storage and handling AN-based fertilizers, even in limited quantities. All three of them deal with straight fertilizer grades of the products as far as known from available information (a certitude in the case of the French and the Spanish cases, for which we also know that the products had passed the EU detonation test).

From information available in open literature [40], the storage in *Saint-Romain-en-Jarez* involved only 3–5 t of 33.5% straight AN fertilizer in big-bags. The building comprised storing cells, including a refrigerated sector and a dwelling section. Storage conditions were quite inadequate (but perceived as correct by the owner just by lack of safety information) compared to state-of-the-art in matter of risk prevention. At least, a noticeable potential for contamination in case of a fire was existing due to piles of plastic cases lying nearby the fertilizer stocks. A very large fire scenario was engulfing the storage area when the detonation of the ammonium nitrate took place, some 60 min after the building had caught fire.

Fortunately no fatality resulted as an immediate consequence of the accident, but the fire service had three staff members heavily injured during the fire fighting operation. Nobody in the emergency team present was aware of the existence of the ammonium nitrate stock before the explosion. Fig. 2 gives a view of the building (including the AN fertilizer storage area) after the disaster.

The two latter records deal with road transport accidents with similar quantities of AN straight fertilizers (20–25 t), packaged in bags at least in one case. At time to press, only limited and partially controllable information have been made available. However, it is clearly established that the two scenarios belong to the type ‘explosion following a fire’. The *Barracas* scenario [41] is due to a collision of the truck with another vehicle, the crash being responsible for the initial fire. The truck went out in the ditch, where the fire is likely to have induced significant contamination between the fertilizer and



Fig. 2. Ruins after the accident at Saint-Romain-en-Jarez (2003), France.



Fig. 3. View of the crater following the AN truck explosion in Romania (2004).

the fuel of the vehicles. The explosion was reported to have occurred some 30 min after the crash.

The latest record of interest in Table 3 has been officially recorded by NIMIC<sup>2</sup> and was largely covered by local press media, as identified as a major disaster in Romania (18 fatalities and significant construction damage). Fig. 3 illustrates the level of damage that occurred from a single truck AN fertilizer load. In that accident, the deaths of the local police chief officer and several firemen were deplored. Noteworthy to notice, the scene was witnessed by many people along the road during the emergency response time (including reporters). One of the reporters was taking a video when the explosion occurred. It was at least partially retrieved by technicians after the event. The information was made temporary available on the web and clearly confirms the presence of two fire locations and the presence of fertilizers packaged in bags.

### 3.3. Further discussion

The preceding events that include three “new explosion events” involving limited amounts of AN-based fertilizers in storage or transportation situations bear some important lessons. The ‘explosion following a fire event’ needs to be given due consideration, even with fertilizer grades of ammonium nitrate, and not only with porous AN. From our literature review, it comes out that a conjunction of extremely unusual conditions is generally thought necessary for a detonation event to happen with fertilizer grades of AN (such as strong energy source, contamination by combustible materials or catalysts, confinement and pressure build-up). Considering low stocks of ammonium nitrate, the EPA document [23] for instance suggests in its ‘hazard awareness section’ that the detonation hazard of low quantities of AN is bound to high confinement, such as those provided inside pipes or

<sup>2</sup> NATO Insensitive Munitions Information Center ([www.nato.int/related/nimic](http://www.nato.int/related/nimic)).

ducts, whereas self-confinement in large pile can constitute localized hazardous areas if conjugated with high temperature. A combination of events such as heating (e.g. in a fire), contamination and serious confinement is also suggested in document [48] as requested to (significantly) increase the risk of explosion. Reflecting perhaps a more recent move in the way the experts shall handle the subject, TNO recently reported that ‘some confinement’ was (only) needed for a risk of ‘explosion following a fire scenario’, at the light of its own analysis of past accidents [43]. Indeed, it is hard to believe, given the description of the previous accidental scenarios involving limited quantities, that in all cases a big confinement favoring an important pressure build-up had actually contributed in the detonation process observed, as a key factor. Also noteworthy to mention in terms of preventive measures, from data reported in Table 3, it seems that the critical time, for a detonation to occur after an initiating fire event lies between 30 min and 1 h. Besides, in all case studies mentioned in Table 3, it is likely that considerable amount of molten nitrate were produced by thermal transfer from the fire which consequently might have suppress, during the course of events, any safety technical barrier provided by the control of porosity, or solid particle size from the process. The behavior of molten ammonium nitrate or product issuing ‘self solidification’ are topics of interest for research for a more detailed understanding of the behavior of such products in accidental scenarios. The determination of the sensitizing degree of the various potential contaminants (organics, chlorides, metals and metallic salts, . . .) would also contribute to scientific-sound analysis of the hazardous processes. This aspect is most important for small capacity storage of AN fertilizers, as, in this case, contaminant sources are there more difficult to handle in terms of prevention.

More globally, technicians must recognize that there are still several significant gaps in our knowledge, due to the extreme complexity of ammonium nitrate and its derived fertilizer preparations, as well as related danger scenarios. Indeed, with this product, we are far from being able to predict, by modeling work, precise indication of modes of explosions given a initiating event (side fire, shock wave, . . .), or for instance, to determine with desired accuracy safe distances between piles of AN products in a divided large storage against sympathetic detonation.

#### **4. The standardization and regulatory framework pertaining to AN-based fertilizer storage: what performance?**

In-depth examination of existing and projected regulatory texts covering safety issues of AN-based fertilizers lies beyond the scope of this paper (see document [44] for updated supplements). This context actually encompasses many official and guidance documents of both national and international applications and moreover is fast

moving as the aftermath of the Toulouse and the WTC disasters.

Based on known evolution fixed at end of 2003, we just try to bring in this section some lighting as regards the way the regulatory scene today supports the control of the risks in storage premises.

##### *4.1. The European Regulation framework status*

The European Economic Community (preceding the European Union) started to regulate the production of AN fertilizers in the 1980s. Until recently, the European legislative framework pertaining to the storage of ammonium nitrate fertilizers was essentially relying on a series of very technical directives (e.g. EEC 76/116, EEC 80/876, EEC/87/94, EEC 77/535) and through the so-called Seveso II directive [45], issued in 1996, where ammonium nitrate is covered as a named substance.

Quite recently, the European Parliament and Council decided to repeal the former first series of Directives pertaining to ammonium nitrate fertilizer safety and to replace it by a single legal instrument in the form of a new regulation: ‘Regulation (EC) no. 2003/2003 of 13 October 2003 relating to fertilizers’ published on the 21st of November same year [2].

Table 4 summarizes the essential features of the European, regulatory background of interest.

The only drastic evolution in terms of control of storage premises comes from the introduction in the *Seveso II* directive of the entry regarding ‘off-spec’ AN products (including fertilizers not passing the EU detonation test) with enforcement of related safety requirements for any storage of that type as soon as 10 t (low level) to 50 t (upper level).

In addition to this overview of the European scene, we present in following subsections (see Section 4.2 and related tables) main features of a selection of national regulatory texts and related guidance documents issued by countries. As the aftermath of the Toulouse accident, this simply means that such products are treated in the context of the *Seveso II* directive as high explosives, not simply as oxidizers. The new European Regulation is quite useful to improve the specifications, traceability and labeling of all type of fertilizers including AN-based products, put on the market in the European Union. However, it is solely a quality driven standard and it does not bringing any risk control tool in storage facilities per se. The main observation of the European legal framework is that stringent safety provisions are only ensured (and controlled by the legislator) only for very large warehouses of AN-based EC fertilizers, that is likely to say on a very limited portion of existing storing premises concerned. In addition, European countries have also to comply with international regulations applying for transportation to or between storage sites, AN-based fertilizers transportation procedures having more specifically to satisfy with UN/ADR class 5.1 (high dosage in AN) or to class 9 (compound fertilizers) products rules.



Table 4  
Core regulatory texts at European level with recent updates for AN products

Designation	Reference	Comments on safety provisions	Triggering values for storage control (t)
Seveso II directive	European Directive EC/96/82	Storage control for two types of AN products Technical grade of AN (>80%) and AN hot solutions (>90%) Fertilizers, straight/NPK with AN > 80%	350/500 1250/5000
Seveso II directive as amended 16 December 2003	European Directive EC/2003/105	Reinforcement of storage control through new scheme with four entries for AN-based products (1) AN fertilizers liable to bear SSD <sup>a</sup> with following characteristics 45% < AN content < 70% and combustible < 0.4% C or passes detonation test Or AN content not more than 45% with unrestricted combustible part (2) AN fertilizer grade passing the EU detonation test, with following specifications >70% AN Or >45% AN with ammonium sulfate Or >80% mixed with inert material (dolomite or limestone) of more than 90% purity (3) AN technical grade or solutions with given additional specifications (4) 'Off-spec' <sup>b</sup> AN and fertilizers not fulfilling EU detonation test	5000/10000 1250/5000 350/2500 10/50
New European Regulation on fertilizers	Regulation of European Parliament and Council 2003/2003 of 13 October 2003 [2]	Consolidation and reinforcement of previous rules applying for EC fertilizers as previously distributed in more than 20 former European directives (most of which have been repealed), e.g. New community rules for the identifications and labeling of the products Detonation test made mandatory for AN fertilizer (straight or compound) of high (28%) content in nitrogen	None (product quality driven safety rules)

<sup>a</sup> Self sustained decomposition.

<sup>b</sup> Not (or no more) meeting product quality specifications.

#### 4.2. An insight of some national regulations and guidance documents pertaining to AN fertilizers safety issues

A brief examination of other important official texts of national scope, regarding the storage of AN fertilizers, leads again to fairly different statements, as can be established from the following section.

##### 4.2.1. The context in France

The statement that only very large warehouses of AN fertilizers are currently controlled by law enforcement is clearly valid for France, which is however the greatest end-user of straight AN-based fertilizers in Europe (see Table 5). There is no longer notification (so called 'declaration') procedure for medium sized storage premises and the 'authorization' procedures (in accordance with lower (respectively, upper) limits defined in the *Seveso II* directive), only start with quantities of AN fertilizers larger than 1250 t (respectively, 5000 t). The scheme is thus in close agreement with the European framework as implemented by the *Seveso II* directive.

##### 4.2.2. The situation in Germany

The German regulatory scene is basically driven by two official documents, namely:

- Gefahrstoffverordnung – Anhang V Nr2 dated January 2000<sup>3</sup>;
- Technische Regeln für Gefahrstoffe: ammoniumnitrat – TRGS 511<sup>4</sup> release June 2004.

Indeed, very low threshold values of products apply in Germany for the control of AN-based fertilizers storage premises. Related safety measures are defined by reference to the categories indicated in Table 6. Requirements for group A (see Table 7 for more information on defined sub-groups) are very severe.

As can be seen in Table 8, safety (minimum) requirements apply for quantities as low as 100 kg for type A products and as low as 1 t for any other type of AN containing fertilizers. This is reported to be linked to some historical reasons (e.g.: the aftermath of the *Oppau* tragedy that killed more than 500). In

<sup>3</sup> Regulation on dangerous goods, Annex V, no. 2.

<sup>4</sup> Technical rules for dangerous goods, ammonium nitrate.

Table 5  
French regulation scheme applying to AN fertilizers storage

Designation	Reference	Comments on safety provisions	Triggering values for storage control
NFU 42001 Amendment 1 [34]	Decree no. 80–478 of 16 June 1980	Provides specifications for AN straight fertilizers, in accordance with former EC Directive 76/116/EEC for EC labeling	None (quality driven standard)
French Legislation on so called 'Classified Installations' (ICPE)	'Code de l'environnement'  Livre V, titre 1 <sup>a</sup> (formally law of 19 July 1976)	The so-called 'nomenclature' (decree of 20th of May 1953, as amended) includes in current version 2 entries regarding the control of AN  Rubrique (entry) 1330: covers AN, including fertilizer grades not complying with NFU42001 as well as hot solutions of AN >90%	Notification (D): 100–350 t. Authorization: 350 t (low), A; 2500 (high), AS
French Legislation on so called 'Classified Installations' (ICPE) <sup>b</sup>	(id)	Rubrique' (entry) 1331 straight AN fertilizers (complying with NFU42001) and compound fertilizers	No notification (D) frame. Authorization: 1250–5000 t, A; >5000 t, AS

<sup>a</sup> Code for the Environment, Part 1, Section 1.

<sup>b</sup> A move to more stringent rules is, however, very likely to occur (under discussions) justified at least by local case histories and French market features.

Table 6  
Risk categorization principle of AN-based products according to the German law

Group designation	Typical risks of related AN-based products
Group A	Detonation risk bound to high content in nitrogen (>70% of AN and more)
Group B	Compound fertilizers: main risk assumed being self sustained decomposition in case of thermal stress
Group C	Thermal decomposition with release of nitrogen oxides
Group D	AN fertilizers in solution, not actually dangerous except in dry phase (latent detonation risk)

Table 7  
Sub-classes of AN-based fertilizers of group A products according to German regulation

Sub-category of Group A	AN content limits (%)	Equivalent N limits (%)
A I	>90	>31.5
A II (straight) + inert materials	80–90	28–31.5
A III: mixtures AN + ammonium sulfate	45–70	15.75–24.5
A IV (compound) + inert materials	70–90	24.5–31.5

addition, it shall be also noticed that in the German regulation, straight AN fertilizers, if not covered by group A (due to AN content less than 80%) shall be considered for classification into C (sub-group C1), if AN content is equal or over 10%.

Table 8  
Essential product limits applying for the German regulation for ammonium nitrate storage

Category of product	Type of requirement	Triggering limit
Group A	Conditioning in bags	Any quantity! (minor exceptions)
Group A	Common set of safety requirements (e.g.: minimum safety distances with combustible = 10 m, access control provisions)	100 kg
Group A	Determination of safety distances	1 t
Group A	Additional safety requirement and permit needed	25 t
Groups B, C and D	Common set of safety requirements	1 t

#### 4.2.3. Regulation in the Netherlands

A classification of AN-based fertilizers (3 main groups A, B and C, according to assumed decreasing hazards) applies, according to rules implemented in official document CPR 1E [46]. The safety measures that apply are defined according to a case-by-case study. Accordingly, there is no general threshold quantity of AN fertilizers that has to be considered (apart from implications of the Seveso II directive, as amended). A recent analysis was made by van der Veen and Müskens [47] providing an overview of the full chain value of AN fertilizers in the Netherlands. In their review, they claim for an update of the CPR-1 local directive.

#### 4.2.4. The regulatory status in the United Kingdom

In the case of ammonium nitrate fertilizers, an early guidance document (however, today outdated as regard the regulatory context description) was produced by the administration suggesting the implementation of basic precautions for AN storage, to consider by users for quantities in store (see Table 9) as low as 50 t, for low dosage, and even only 1 t of products, for high dosage products.

Table 9  
Threshold limits of AN fertilizers for relevancy of HSE guidance on AN storage in the UK [48]

Category of AN fertilizers	Triggering limit for application (t)
AN-based fertilizers with N > 28%	1
AN-based fertilizers with N < 28%	50

On the current UK regulatory scene, specific legislation applies for large quantities (greater than 1000 t) which converts the European framework on the national level (e.g. the Control of Major Accident Hazards Regulation 1999 (COMAH) and The Planning (Control of Major Accident Hazards) Regulations 1999). A more recent move is the amendment, in December 2002 of the Notification of the Installations Handling Hazardous Substances Regulations 1984 which now applies to all sites which store more than 150 t (reduced from 500 t) of AN-based fertilizers with a total nitrogen content greater than 15.75% (changed from greater than 28% from AN). The exemption previously valid for EC fertilizers has also been removed as a result of this amendment. This is clearly a consequence of the Toulouse accident. The UK administration anticipated that the aforementioned modification might impact some 5000–6000 storage sites at farmhouses and some further 400 storage premises of other types (e.g. pertaining to agricultural merchants).

#### 4.2.5. Miscellaneous information of interest from other countries

The USA have no real specific legislation for the control of hazards coming specifically from the storage premises of AN-based fertilizers at the federal level, but the National Fire Protection Association has been regularly updating its *Code for the Storage of Ammonium Nitrate* since 1965 [16]. The code covers safety issues for AN fertilizer grades, straight and compounds, in quantities of more than half a short ton (about 500 kg) provided that the AN content is at least 60%.

The risk of unlawful use of explosive derived from AN-based fertilizer grades has motivated countries like Ireland, Belgium or China, to forbid the use of AN straight fertilizers with high nitrogen content (more than 27.65% in Ireland [49]).

In Canada, a specification regulation applies for the storage premises of ammonium nitrate-based fertilizers of more than 60% that are in use for the national rail transportation framework. The regulations apply for storage capacities exceeding 1500 kg. A permit is required for storage capacities exceeding 200 t. However, general rules applying to AN storage at Federal level in Canada (going to move, as reported at the *Ispira* workshop [31]) are only applicable currently to large facilities (more than 1000 t).

Sweden has also implemented some restriction concerning the handling of AN-based fertilizers, such as a permit required above a quantity of 10 t of product. Switzerland authorities do have some control on the storage facilities with ammonium nitrate quantities exceeding 20 t.

#### 4.2.6. Regulating AN storage, a moving issue

The preceding overview of the regulatory context was prepared taking into account the known official texts published by end of 2003. The authors are aware of on-going discussions at national levels indicating that the regulatory scene will continue to move in the near future in some places (as it is planned in France). As can be seen from the review, the situa-

tion is quite different from one country to another, some countries currently control only very large sites of AN-based fertilizers, while others have implemented much lower threshold limits for incentive or law-enforced control of safety storage practices in medium or low capacity storage premises. Motivation for further moving comes at first, through mandatory requirement for EU member states to transpose EC Directives with a given delay in their national regulatory schemes. Secondly, EU members and non EC members may wish to integrate additional safety or security goals for a further improved control of related hazards, integrating Nation-specific and lessons learnt from the most recent European accidents aspects (see for instance van der Veen's paper [47] for the views in the Netherlands).

Whereas harmonization and progress in control efficiency of AN fertilizers storage through regulations is highly desirable this objective remains challenging, as too restrictive requirements compared to real hazards and related actual risks may indeed work more as a barrier against free trade and circulation of products than as efficient prevention or protection measures.

## 5. Typology of risks related to small storage of AN fertilizers

The importance of the risks presented by small AN-based fertilizers sites may vary to a great extent according to national schemes prevailing for fertilizers distribution (that in turn influences flow-sheet of AN movements as well as intermediate storage site numbers and related average capacities) and on local indoor or outdoor storage practices where small quantities are dealt with.

### 5.1. Trade factors

As previously said, millions of tons of AN fertilizers are produced and distributed all over the world on a yearly basis. Due to seasonal effects, storage are needed at every stage of the chain value of the commercial products, the distribution activity being a more or less complex process, involving export–import companies, state of independent traders, wholesalers redistributing to small retailers, independent or central co-operatives that in turn supply end-users. This scheme may be simplified in a first approach by Fig. 4 indicating implications on storage features from top to bottom of the chain value.

Reality of distributions schemes highly differs from country to country (if not at regional scale). Taking this into account, a variety of situation may be present on the national levels, due to the importance of the market, and to related distribution characteristics. To illustrate this, we have reprocessed and completed (from ref. [53]) in Figs. 5–7 the distributions schemes pertaining, respectively, to France, Germany and Japan explaining how commercially the products move from the producers or import–export companies to the

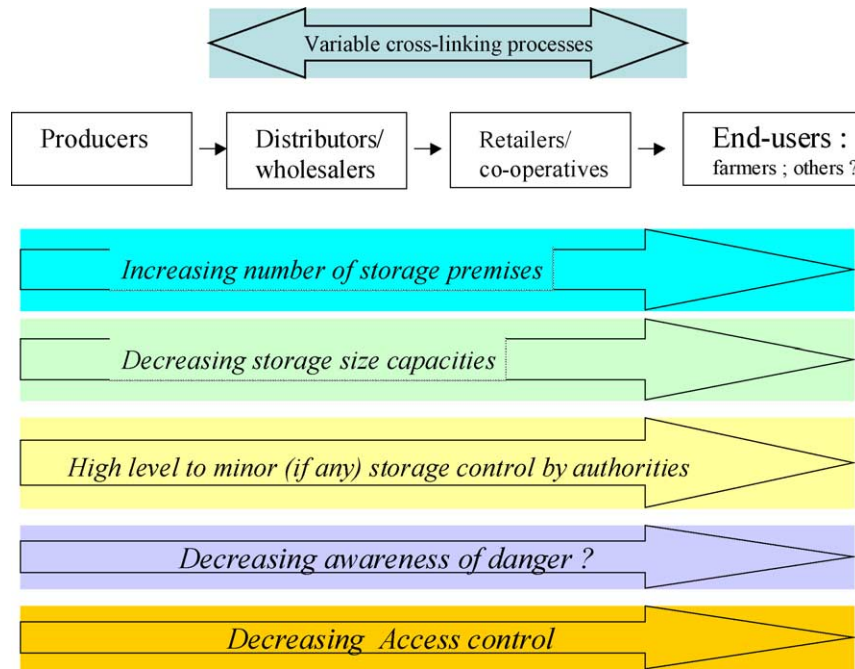


Fig. 4. Economy-driven factors governing AN fertilizers storage.

end-users; other known schemes with related statistics about modes of sales to farmers, forms of deliveries and transport are available for many other important agricultural countries (see ref. [53]).

Fig. 5 pertains to the situation in France, where direct or indirect (through supplying wholesalers) independent trading of fertilizers (including AN fertilizers) compete (more or less with equal market shares) with cooperatives or cooperatives

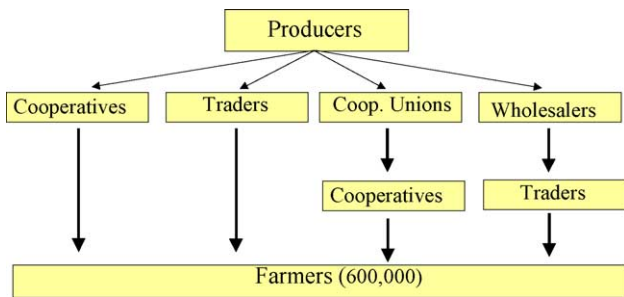


Fig. 5. Distribution of fertilizers in France (1999, after ref. [53]).

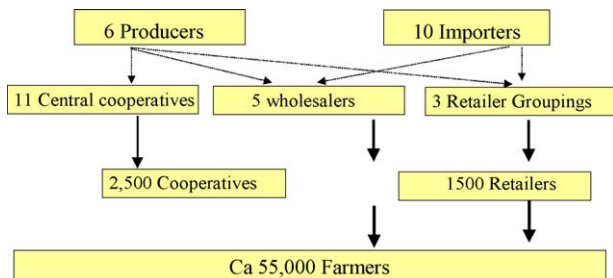


Fig. 6. Distribution of fertilizers in Germany (1995, after ref. [53]).

unions (representing ca 6000 storage sites) to distribute the products to end-users (e.g. some 600,000 farmers).

Due to economical considerations linked to transportation distances, high dosage AN fertilizers (mainly 31.5 and 33.5% N), in bags or in bulk, are the main product distributed and stored in France (the largest European market in Europe). Storage premises too small to require notification to the authorities (e.g. under 1250 t up to mid 2004) exist in significant numbers at both cooperative levels (in so-called “silos” sites) and at end-users’. That is to say, by reference to Fig. 5, at the level of the two last stages in the distribution scheme (cooperatives + traders and farmers).

Similarly, the comparative situation for Germany is given at Fig. 6, that points out the existence of a small number of

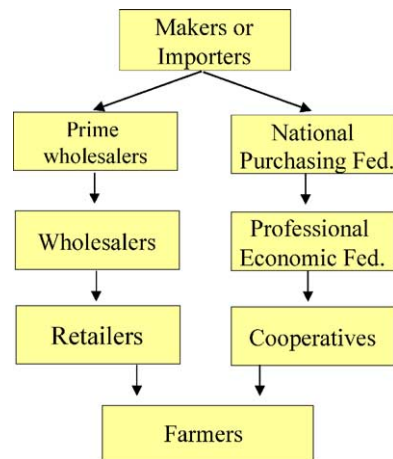


Fig. 7. Commercial flow-sheet for fertilizers in Japan (after ref. [53] – 1999).

producers and importers as supplying sources, a first level key distributors of three different types (from business organization point of view), the activity of which relies on the operation of a limited number of medium or large size capacity storage premises. Like in France, a second level of cooperatives and retailers centers are ultimately delivering the products to some 55,000 farmers. A major difference from the French market is there the type of AN fertilizers dominating the market: namely low dosage AN-based fertilizer, therefore with more limited accidental detonation potential. This a result of the very stringent regulatory scheme existing in Germany.

Fig. 7 refers to the distribution scheme applying to Japan. Japan has still a more staged distribution chain from producers (or importers) to end-users, but the main statement keeps that at the end of the chain, numerous storage of AN fertilizers of limited capacity are involved. Contrary to what apply in previous examples the form of delivery to farmers in Japan, as well as intermediate destinations is nearly in totality in bags (loose or palletized).

Ninety percent of the distribution flux to the end-users comes from the cooperatives against only 10% from independent retailers.

## 5.2. Technical factors

Whereas fairly well known and rather well controlled in dedicated AN stores in large facilities, low capacity stores of ammonium nitrate, the risk of potentially hazardous co-storing of AN fertilizers with incompatible materials is clearly a concern in small storage facilities. It is well known by the scientific community that many chemical substances, when present even in minor quantities in technical grades of AN, or when stored in close proximity of AN products may lead to hazardous reactions associated with exothermic reactions and/or emission of (toxic and/or flammable) decomposition products. From ref. [6], the list of materials to avoid at user's site of AN fertilizers encompasses namely: combustible materials (see Table 10 for a broad lists of such potential materials of organic nature), reducing agents, acids, alkalis, sulfur, chlorates, chlorides, chromates, nitrites, permanganates, metallic powders and substances containing catalytic metals such copper, nickel, cobalt, zinc and their alloys. Therefore, it is important to notice that many (if not all) end-users of AN fertilizers (e.g. crop producing farmers, fruit tree producers, wine-growers, . . .) have obvious professional usage of many of those undesirable products inside AN fertilizers storage buildings. For instance, cattle growers may have to order, use and store plastic drums of concentrated sodium hydroxide solutions for treatment of sheep or cows affected by some contagious diseases (use in the form of diluted feet baths).

Other end-users of fertilizers, such as winemakers, use large quantities of sulfur-based fungicides for seasonal treatment of grapes.

Table 10  
Examples of common organic contaminants (after ref. [16])

Products
Animal fats
Baled cotton
Baled rags
Baled scrap paper
Bleaching powder
Burlap of cotton bags
Caustic soda
Coke
Charcoal
Coal
Cork
Camphor
Excelsior
Fibers of any sort
Fish oil
Fish meal
Foam rubber
Hay
Lubricating oil
Fish meal
Linseed oil or drying oils
Naphthalene
Oakum
Oiled clothing
Oiled paper
Oiled textiles
Paint
Straw
Sawdust
Wood shavings
Vegetable oil

Technical grades of sodium chlorate, another common incompatible product is still in important use for farming and gardening as a non-selective and cost-effective total herbicide. Other common incompatible products in use on a more general way in agriculture associated with potential problems may be wood stacks, hay piles, organic fertilizers and plastic packing cases.

On the cooperative or retailer sites, often all types of products and equipment needed by farmers are generally delivered in a single distribution center. That is to say that precautions against incompatibilities between different stocks are requested.

As occasional safety auditors of premises of retailers and cooperative type distributors of products for the agriculture on the French scene, the authors may attest that piles of pesticides (including solid or liquid sulfur fungicide bags or drums, and sodium chlorate drums), and fertilizers of all sorts are routinely present in adjacent buildings (if not stored at small retailers' sites in same non compartmented storage surface inside a single warehouse). The situation occurs where quantities of AN fertilizers involved may be in the range of some tens of kilograms (small deposits in local 'silos' belonging to major French cooperatives or small retailers' stores) to several hundreds of AN fertilizers in bags, and even to some thousands of kilograms on sites where AN fertilizers are present both as bulk and packaged products.

Some reasons explaining the situations are:

- investment capacities mainly devoted to repair and minor modification of available built environment due to low economical margins;
- seek for maximal flexibility;
- willingness to optimize the use of space in terms of overall capacity against segregation principles favoring safety but being 'storage surface' consuming;
- remaining stocks needing 'attic' room as nobody actually cares to manage the problem more pragmatically (e.g. by recycling the products, treating them as wastes, transferring them to another dedicated site . . .).

End-users sites are facing inherently co-storing potential problems together with the additional constraints related to abrupt (seasonal) changes in needs for storage space that very often lead to 'sharing' or turn over of storage cells, giving undesired opportunities for repeatable contamination risks. Frequency of fire incidents is quite important and well known from insurers there also, increasing the risks of a fire affecting unknown stocks of AN fertilizers from a statistical point of view. Indeed, most of identified potential contaminants such as wood, wood shavings or dusts, plastic cases or bags, organic materials from cattle, hay, seeds . . . , are never very far from fertilizers.

### 5.3. Human factors

Here is a last key factor that has to be taken into consideration. For instance, in relation with a previous technical point, arson is known as a quite important cause of farm fires [11]. The farmer as an end-user is probably the less aware of the hazardous properties of the product for two main reasons. Due to his professional activity, education and training in management of risks associated with so-called dangerous chemicals and associated danger scenarios is quite often very limited. The knowledge as associated to the information provided about the hazards pertaining to the products quite naturally diminish from the manufacturing site to the end-user sites. Better training of end-users by appropriate and dedicated means is thus highly desirable.

## 6. Small deposits of AN fertilizers and the security problem

The significant rise of the terrorism threat is also a matter of concern, say since a decade, with the 11th of September 2001 marking a symbolic date of course, throughout the world. In that context, the misuse of straight AN and other nitrate containing fertilizers for preparing unlawful explosives have been identified in a number of well-known terrorist attacks (Nitro-urea was used for bombing the World Trade Center in 1993 [54], AN fertilizer was reported as the key explosive ingredient in the Bali attack in 2002). We reported earlier that such considerations were a motivation for spe-

Table 11

Australian licensing procedure characteristics (compiled from [52])

AN related activity	Threshold limit (kg)
Transport	20
Business storage (manufacturer, mining industry, suppliers, importers and exporters, . . .)	3
Activity at farm	Any quantity

cific legislative texts in some countries (see Section 4.2.5). Much more recently, several thefts of AN-based fertilizers – but also true high explosives – have been reported by the media in several countries leading to recent new focus by some authorities on this issue. The more recent move seems to originate from Australia.

Indeed, two different ways seem to be explored to control the threat as regard the case of ammonium nitrate that is not desirable to comment further. On the one hand, a technical issue (a real challenge?) is to develop "desensitized" AN-based materials for use as commercial fertilizers in a way that it would be very difficult for terrorists to reuse the resulting products: this is for instance the route followed in China and promoted by law enforcement. Such technical development and its current local perspectives were recently presented at the latest meeting of the OECD-IGUS group of experts [50] in Ottawa, by Dabin [51]. The other way is to consider the topic in the hands of the regulators and the authorities in charge of controlling the chemicals from the manufacturing sites up to the end-users. The Council of Australian Governments for instance recently agreed (June 2004) to create a licensing procedure for a better control of security issues regarding ammonium nitrate [52]. In practice, it is planned to implement in all Australian states a license for the so-called security sensitive ammonium nitrate (SSAN) that will be needed for those who wish to purchase, store, or transport such products (containing greater than 45% AN, excluding solutions and class 1 explosives) according to threshold values summarized in Table 11.

On a more general way, the weakest link with low capacity storage premises as regard the security aspect might be obviously the lack of access control to those sites, but the overall debate is much more complex. Indeed security issues related to unlawful explosives in the context of terrorism largely exceed the simple misuse of ammonium nitrate issuing from uncontrolled low-capacity storage sites, and moreover many other chemicals may be derived for explosives making.

## 7. Summary and conclusions

Low-capacity storage of any given commercially important products are generally more important in number than large dedicated warehouses. Handling properly safety and security aspects in those facilities when hazardous products like AN-based fertilizers are dealt with remains a challenging issue for regulators as well as operators.

Small operators of AN storage premises (retailers, end users at farmhouse, . . .) might simply not follow the rules (when any applies!), just by ignorance or by misunderstanding of inadequate legislation framework, whereas real threats may be present, due to the overall activity aside the AN stocks. However, actual fire and explosion risks pertaining to storage of AN-based products, as illustrated by our review of accidents, are not limited to large dedicated warehouses. The explosion of ‘off-spec’ AN products in Toulouse, was recently followed by unexpected accidents with ‘true’ AN fertilizers in limited amounts that have raised new or at least underestimated safety issues with the product. Most of them (if not all) have taken place in Europe (France, Spain and Romania), at least two of them having involved ‘EC marked’ or quality equivalent fertilizers.

All stakeholders in the promotion of safety issues with ammonium nitrate must have in mind that that low capacity storage of AN-based fertilizers still present real dangers in practice, including the risk of mass detonation in specific – but still not completely ruled out – circumstances. We have pointed out that there is a genuine typology of risks related to low storage of ammonium nitrate fertilizers that reveals trade, technical and organizational aspects. Relative importance of those aspects may highly vary from one country to the other.

Furthermore, our analysis is clearly identifying the need for further research on AN-based fertilizers, despite the numerous pieces of work already carried out in the past decades by the profession and various research teams. In particular, aiming at a better understanding of the real course of events that drive from an initial fire (or other great source of energy) to an “explosion following a fire” scenario, including initiation mode and role played by sensitizing agents becomes to our view a priority target.

Meanwhile, technical prevention measures including as a first priority a better information and training of end-users must be studied to promote still safer storage facilities and encourage better storage practice at end-users’ sites. It must indeed be postulated that most of the end-users (farmers) are far from having in mind what the dangerous properties of fertilizers are, and very few know in particular what type of basic phenomena would affect AN products in the vicinity of a fire (such as liquefaction trend). Security issues with AN – not necessarily bound to low capacity storage of the product – have also been briefly commented, given the rising concern of terrorism background.

Reinforced control of low capacity AN-based fertilizers storage deserves consideration as another safety barrier to consider in addition, depending on local agricultural trends (e.g. importance of the market, level of use of high N content straight fertilizers, . . .).

## Acknowledgements

The authors thank very warmly Roy Merrifield, from Health and Safety Executive (UK), for his helpful and sig-

nificant comments, especially about the UK regulatory scene and for the editorial advice we receive from him on this paper.

## References

- [1] Guidance for Sea Transport of Ammonium Nitrate Based Fertilizers, European Fertilizers’ Manufacturers Association (EFMA), Belgium, 2004.
- [2] Regulation (EC) No. 2003/2003 of the European Parliament and the Council of 13 October 2003 Relating to Fertilizers, Official Journal of The European Union, L304/1, 21/11/2003.
- [3] Recommendations on the Transport of Dangerous Goods: Model Regulations, 13th ed., United Nations, Geneva/New York, 2003.
- [4] A. Lewis, Loss prevention library of fire safety, Fire Prot. Assoc. 6 (1999).
- [5] A.B. Spencer, G.R. Colonna (Eds.), NFPA Fire Protection Guide to Hazardous Materials, 13th ed., NFPA International, Quincy, MA, USA, 2002, pp. 49–109.
- [6] Ammonium Nitrate “Hazardous Substance Fact Sheet”, New Jersey Department of Health and Senior Services, 1998.
- [7] Weiss (Ed.), Hazardous Chemical Data Book, second ed., Noyes Data Corp., 1986, p. 94.
- [8] Chemical Safety Datasheet, Kluwer Academic Publishers, The Netherlands, 1991, p. 48.
- [9] R.P. Pohanish, S.A. Greene, Rapid Guide to Chemical Incompatibilities, VNH, USA, 1987, p. 54.
- [10] Guide d’intervention des Sapeurs-Pompiers Genevois, Service d’Incendie et de secours, Ville de Genève, third ed., 1987 (in French).
- [11] I. Jerome, The Loss Prevention Library of Fire Safety, vol. 2, 1994.
- [12] J.A. Davenport, Storage and handling of chemicals, in: E. Cote (Ed.), The NFPA Handbook of Fire Protection, 19th ed., NFPA, Quincy, MA, USA, 2003, pp. 6–323.
- [13] EFMA, “Guidance for the Compilation of Safety Data Sheets for Fertilizer Materials, Ammonium Nitrate Fertilizers”, <http://www.efma.org/publications/guidance/section08.asp>.
- [14] V. Dolah, et al., Explosion Hazards of Ammonium Nitrate Under Fire Exposure, US Bureau of Mines (USA), Report on Investigation 6773, 1966.
- [15] T.M. Groothuizen, E.W. Lindeijer, H.J. Pasman, Danger aspects of fertilizers containing ammonium nitrate, in: Dutch Nitrogenous Fertilizer Review, CSV (Central Nitrogen Sales Organization Ltd.), vol. 14, April 1970.
- [16] NFPA 490, Code for the Storage of Ammonium Nitrate, 2002 ed., National Fire Protection Association, Quincy, MA, USA, 2002.
- [17] European Directive 68/548/EEC (as Amended) Concerning “The Approximation of Laws, Regulation and Administrative Provisions to the Members States Relating to the Classification, Packaging and Labeling of Dangerous Substances”, OJ, vol. 196, 16 August 1967.
- [18] European Directive 1999/45/EC (as Amended) Concerning “The Approximation of Laws, Regulation and Administrative Provisions to the Members States Relating to the Classification, Packaging and Labeling of Dangerous Preparations”, OJ, L200, 30 July 1999.
- [19] Global Harmonized System of Classification and Labelling of Chemicals (GHS), United Nations, Geneva, 2003.
- [20] D. Waight, Going global—the United Nations has developed a new globally harmonized system for classification and labelling of chemicals, Fire Eng. J. Fire Prev. (December) (2003) 21–23.
- [21] NFPA 704, Standard System for the Identification of Hazards of Materials for Emergency Response, National Fire Protection Association, Quincy, MA, USA, 2001 (revision).
- [22] NFPA 49, Hazardous Chemicals Data, National Fire Protection Association, Quincy, MA, USA, 1991.
- [23] EPA, Chemical Safety Alert: Explosion Hazard from Ammonium Nitrate, EPA 550-F-97-002d (<http://www.epa.gov/agriculture/ache.html>), December 1997.

- [24] G.T. Atkinson, Generation of NO<sub>x</sub> in Fires Involving Ammonium Nitrate and Other Chemicals, HSL Report FR/01/11, 2000.
- [25] K. Shah, Toxic Fumes Hazards from Fires Involving Ammonium Nitrates, Congress ANNA 2003, Tunica, MS, USA, October 2003.
- [26] V. Christiansen, R. Kakko, B. Koivisto, Environmental impact of a warehouse fire containing ammonium nitrate, *J. Loss Prev. Process Ind.* 6 (4) (1993) 233–239.
- [27] C. Cwiklinski, L'essai en Grand: Une Approche Préventive et Prévisionnelle Pour L'incendie en Milieu Industriel, R.G.S., vol. 97, October 1990, p. 51 (in French).
- [28] G. Perbal, The thermal stability of fertilisers containing ammonium nitrate, *Proceedings of the International Fertiliser Industry*, vol. 124, York, UK, 1971.
- [29] R. Turcotte, P.D. Lightfoot, R. Fouchart, D.E.G. Jones, Thermal hazard assessment of AN and AN-based explosives, *J. Hazard. Mater.* 101 (2003) 1–27.
- [30] S. Duffield, M. Wood, "Workshop on Ammonium Nitrate", 30 January–1 February 2002, European Commission Joint Research Centre, Ispra, Italy, Summary Report (download: <http://mahbsrv.jrc.it/ispra-AN/ispra-AN-general.html>).
- [31] D. Heather, A Review of Past Ammonium Nitrate Accidents and Lessons Learned, EFMA Paper Presented at the "Workshop on Ammonium Nitrate", 30 January–1 February 2002, European Commission Joint Research Centre, Ispra, Italy (<http://mahbsrv.jrc.it/ispra-AN/ispra-AN-overview.html>).
- [32] Accident at Fertiberia S.A. Encombreras Valley, Murcia—Self-sustained Decomposition of NPK 15-15-15 Fertilizers, 26–30 January 2002 (source: Spanish Ministry of the Environment).
- [33] G. Marlair, C. Cwiklinski, F. Marlière, C. Costa, A Review of Large-Scale Fire Testing Focusing on the Fire Behaviour of Chemicals, *Interflam'96*, in: *Proceedings of the Interscience Comm. Ltd.*, London, UK, 1996, pp. 371–382.
- [34] Standard NFU 42 001, Engrais, Dénominations et Spécifications, Amendment 1 AFNOR, 1989 (in French).
- [35] K.D. Shah, Safety of ammonium nitrate fertilisers, in: *Proceedings of the International Fertiliser Society*, vol. 384, York, UK, 2001.
- [36] T. Bourdeaux, C. Michot, M.-A. Kordek, Toulouse disaster 'Grande Paroisse' fertilizer plant – 21 September 2001 – preliminary investigations and overview of damage, ANPSG Meeting, Tucson, AZ, USA, 7–10 October 2002.
- [37] N. Dechy, T. Bourdeaux, N. Ayrault, M.A. Kordek, J.C. Lecoze, First lessons of the Toulouse ammonium nitrate disaster, 21st September, AZF plant, France, *J. Hazard. Mater.* 111 (2004) 131.
- [38] UNEP/APELL, Ammonium Nitrate Explosion in Ryongchon Train Station, North Korea – 22 April 2004, 161 People Killed and 1300 People Injured – Other Accidents Involving Ammonium Nitrate, see [www.uneptie.org/pc/apell/disasters/korea.htm](http://www.uneptie.org/pc/apell/disasters/korea.htm).
- [39] R. Freeman, The Cherokee ammonia plant explosion, *Chem. Eng. Prog.* 71 (11) (1975) 71.
- [40] R. Dosne, Explosion d'ammonitrates dans un bâtiment agricole, *Face au Risque* 399 (2004) 26 (in French).
- [41] J.-L. Claret, L'argus des accidents technologiques, *Préventique Sécurité* 76 (2004) 68 (in French).
- [42] NIMIC Newsletter, second quarter 2004, NATO Publication, 2004 (<http://www.nato.int/related/nimic/newsletter/news.htm>).
- [43] R.J.A. Kersten, W.A. Mak, Explosion hazards of ammonium nitrate, how to assess the risk? in: *Proceedings of the International Symposium on Safety in the Manufacture, Storage, Use, Transport and Disposal of Hazardous Materials*, Tokyo, 10–12 March 2004.
- [44] D.J. Heather, H. van Balken, Review of recent legislation affecting the fertiliser industry, in: *Proceedings of the IFS*, vol. 534, York, UK, 2004.
- [45] European Directive 96/82/EC, As Amended (so-called Seveso II) on the Control of Major-industrial Hazards (see also: <http://inovvator.jrc.it/downloads-pdf/Seveso2-Directive.pdf>).
- [46] Document CPR 1E, "Nitrate-Containing Fertilizers – Transport and Storage", Committee for the Prevention of Disasters caused by Dangerous Substances, third ed., Directoraat-Generaal van de Arbeid, The Netherlands, 1982.
- [47] H. van der Veen, P.J.W.M. Müskens, Environmental risks associated with activities involving ammonium nitrate in The Netherlands, VROM Paper at Sixth International Conference on Environmental Compliance and Enforcement, Costa-Rica, 15–19 April 2002.
- [48] Storing and Handling Ammonium Nitrate, HSE Guidance, IND(G)230L – C100, December 1996 and revised edition 2001.
- [49] Explosives, Control of Ammonium Nitrate, Ammonium Nitrate Mixtures and Sodium Chlorate, Statutory rules and orders of Northern Ireland, vol. 118, 15 May 1972.
- [50] OECD IGUS web site: <http://www.oecdigus.org/>.
- [51] L. Dabin, et al., Inactive Modification of Ammonium Nitrate and the Determination of its Activity as Oxidiser in Explosives, Oral Communication from the Nanjing University of Science and technology of China (also presented at the OECD IGUS-EPP 2004 Meeting hosted by CANMET-NCR, Ottawa, 19–21 April 2004).
- [52] Department of Infrastructure Energy and Resources (Australia), Australian (Proposed) Regulation on AN Storage, <http://www.wst.tas.gov.au/attach/stagn2.pdf>, 2004.
- [53] K.F. Isherwood, Mineral fertilizer distribution and the environment *Int. Fertilizer Ind. Assoc. (IFA)*, Paris (2000) (<http://www.fertilizer.org>).
- [54] W.E. Manning (Ed.), *The World Trade Center Bombing: Report and Analysis*, FEMA, US Fire Administration, Technical Report Series, vol. 076, 1995.