Lessons learned from major accidents involving fertilizers

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Summary

This paper presents the results of the analysis of 25 major accidents involving fertilizers in the European Commission's major accidents reporting system (the so-called eMARS) and other publicly available sources, including also road traffic accidents. Ammonium nitrate (AN) has been involved in numerous accidents causing explosions, fires, and releasing toxic fumes, and it is known that even small scale storage of ammonium nitrate fertilizers (defined as low as 10 tonnes in some legislation) may place the population at high risk if proper safety measures and procedures are not fully in place.

Keywords: fertilizer, major accidents, lessons learned, decomposition

Introduction

Ammonium nitrate was first produced in 1659. It is a "dual-use" substance from which either fertilizers or explosives can be produced. It is produced at a large scale throughout the world (over 20 million tonnes in 1998) with over a third of this production based in Europe (over 7 million tonnes in 1998). It is without doubt important for industrialized society. Even though pure ammonium nitrate is generally used safely, accidents involving fertilizers have occurred over the years (Figure 1). Figure 1 depicts the fatalities and tonnage associated with AN accidents identified by this study from 1916 until present. The accidents presented illustrate that even small storages of ammonium nitrate fertilizers, defined as low as 10 tonnes in some legislation, may place the population at high risk if proper safety measures and procedures are not fully in place. The most notorious event that also contributed to the modification of the Seveso II Directive[1] was the Toulouse accident in 2001. The investigation on this specific event was published in recent LPB[2, 3] as well as other sources[4, 5, 6]. The three major phenomenon associated with ammonium nitrate are fire, explosion and decomposition. Contamination of ammonium nitrate, for example with hydrocarbons or other oxidizing agents[7] can increase the sensitivity of the fertilizer. Contaminated ammonium nitrate can decompose along a lower energy pathway than pure ammonium nitrate[8, 9]. There are substances that are incompatible with ammonium nitrate[10, 11] and they can affect the temperature of decomposition of the ammonium nitrate. Furthermore, as an oxidizing agent, ammonium nitrate can intensify the development of a fire involving combustible materials (like wood or plastics)[12] as well as moisture — as it outlined later in Case 2.

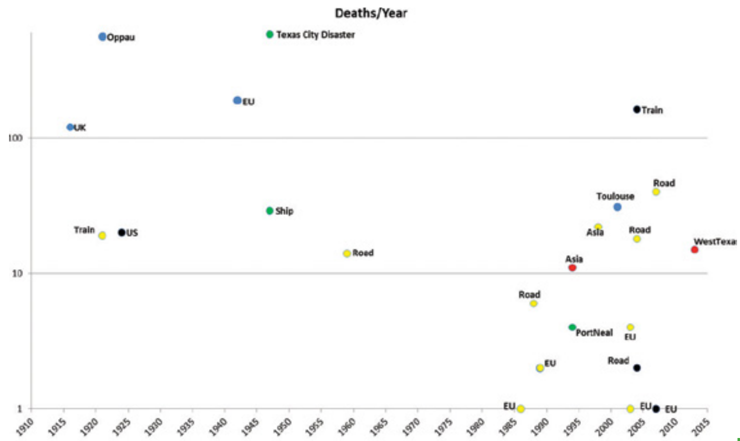

Figure 1 – Examples of ammonium nitrate accidents [6]

Selection of the case studies

Events were chosen on the basis that either ammonium nitrate or NPK fertilizer (nitrogen, phosphorus, potassium) was involved in the accident. Most accidents generally occurred in warehouses or chemicals manufacturers, but road traffic accidents involving ammonium nitrate fertilizers have also caused serious accidents resulting in severe casualties and property damage. The elevated risk to the population and first responders was due to insufficient fire prevention and a lack of protection and control systems. In at least six cases, there was a lack of knowledge of the inherent hazards associated with handling and storage of ammonium nitrate fertilizers. In 14 cases, decomposition was the main cause and this potential phenomenon of fertilizers was not considered as a hazard. Wooden pallets were allowed to be stored in the affected warehouses in four cases, as was the situation in West, Texas in 2013[13]. In many cases, the operator had not established appropriate practices for controlling the hazards associated with the presence of ammonium nitrate and dangerous substances. In four cases, fertilizers were stored

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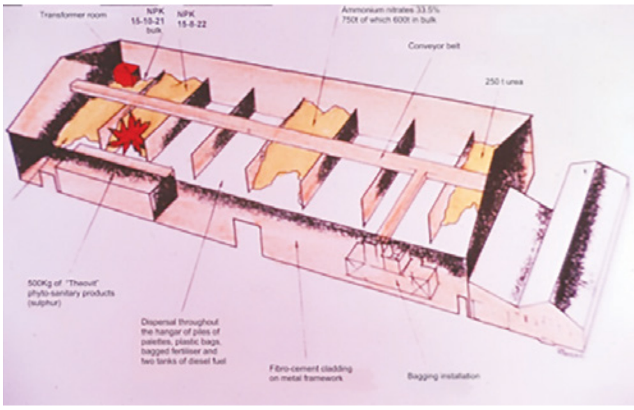

Figure 2: The installation concerned[14]

in one compartment in quantities exceeding the standard threshold established to avoid creating conditions favourable to the self-decomposition that subsequently occurred. There were also four cases where storage conditions allowed contaminants to be introduced into the ammonium nitrate, greatly increasing the risk of the massive fire that eventually occurred at each location. Additionally, some accidents are notable for the failure of the authorities to recognise and intervene regarding the significant exposure of surrounding populations and business to risks associated with nearby ammonium nitrate installations. In many cases one or more elements of the safety management system required improvement.

In particular, it was found that awareness of ammonium nitrate hazards and training on associated safety procedures for employees was either woefully inadequate or nonexistent in the establishments where eight of the accidents occurred.

Case 1

A fire occurred in a warehouse storing fertilizers and chemical products. The storage installation was subdivided into eight compartments, of which two contained NPK (15% N, 8% P, 22% K) fertilizers in quantities of 600 tonnes and 850 tonnes respectively. One compartment also contained 650 tonnes of ammonium nitrate fertilizer and the other was also storing 200 tonnes of 46% urea solution. On 29 October 1987, smoke was detected by an operator in Box No. 2 of the warehouse, i.e. the compartment that contained 850 tonnes of NPK fertilizer[14]. The first reaction of the personnel was to attack the source of the fire with portable fire extinguishers, in the absence of activated fire hose reels. The intervention of the firefighters appeared to focus solely on the presence of ammonium nitrate fertilizer, ignoring the nature of the other chemical products. The accident resulted in the slight injury of three employees and 38,000 people were evacuated for eight hours.

Due to the conditions of transport (in the holds of a ship that had previously stored wheat) and the storage conditions (on a bed of sawdust to dry the floor of the box), the fertilizer became mixed with organic material. Also, it was found that defective, poorly insulated power cables were near the fertilizer pile. Furthermore, wooden pallets were in contact with the fertilizer compounds. These compounds then caught fire during decomposition and released heat, accelerating the decomposition.

The NPK fertilizer had been unloaded the day before the accident and completely filled the capacity of the storage compartment. At the time no abnormalities in the product (e.g., caking) were observed, although the temperature at the time (40° C) should have been identified as a cause for concern. Furthermore, the electrical installation of the site was old and other potentially unsafe conditions were present, such as lack of insulation, incomplete grounding, oversized circuit breakers as identified by a private verification in a 1986 report. (No repairs were conducted as follow-up to the report.) The zone in which the fire started was located below the electrical cables that hung beneath the transport motor. Finally, there was no effective means of firefighting in place, such as a water riser or a self-propelled fire hose.

Lessons learned

- Appropriate extinction equipment for the products stored must be available to personnel trained in the prevention of risks, the detection of abnormalities and in emergency response. In this case, the personnel of the establishment were not aware of the risks associated with fertilizer and only had powder extinguishers which are ill-adapted to this type of fire. No water extinguishing equipment or fire hose reels were available on the site.
- A sound characterisation of the risks involved, particularly involving an understanding of dangerous materials implicated is indispensable for implementing efficient fire prevention and fire-fighting plans. Doubtlessly the loss of information concerning the nature of the products involved in the fire played a major role in the development of the incident. In the absence of characterisation of the products present and thus of the risks involved, disagreements between experts occurred which delayed an effective response. Furthermore, the establishment was not classified by the fire department and was not subject to an emergency plan. It is essential that each emergency centre should hold an inventory of potential risks for its sector of intervention to enable efficient response from the moment that the alarm is given.
- Effective response requires also that there should be adequate and permanently available sources of water including, for example, when the tide is going out.

Case 2

Self-decomposition of NPK fertilizers led to a fire in a storage silo and release of toxic substances, mainly nitrogen oxides. The silo contained approximately 15,000 tonnes of the product, but the fire was detected early enough (probably from the fumes rather than automatic detection) to avoid serious consequences. Five firefighters were treated for minor injuries in hospital and some onsite personnel suffered from eye and throat irritation and burning. Some neighbouring establishments and houses were evacuated and other areas were told to shelter-in-place. No offsite injuries were reported. The fire was controlled after most of the material was removed by mechanical means.

It was thought that exposure to moisture had caused caking in a portion of the product. In addition, the product may have been in contact with organic material, specifically, pigeon

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excrement, due to the considerable quantity of pigeons present in the silos. Over a two-month period, some of the product involved in the accident had been exposed to ambient conditions during a period in which the region experienced a lot of rain. Self-sustaining decomposition caused by the presence of a contaminant would probably have been accelerated by the presence of anomalous crystal structures (caking) in the product. Leaks in the silo roof caused water to fall on the exposed lot, generating a possible recrystallization or caking of the fertilizer. There was no documentation available at the installation reflecting the possibility that such an accident could take place. Also, a large amount of the NPK was stored in the same location without proper separation. This practice was actually counter to company practice regarding storage conditions.

Lessons learned

- Storage facilities should strive to eliminate the possibility that impurities can be introduced into the ammonium nitrate. Preventive measures should be in place to prohibit birds and animals from contact with the product or, if this is not possible, ammonium nitrate should not be stored in that facility.
- In storage of ammonium nitrate compounds, exposure to water should be avoided in order to prevent caking which can accelerate oxidisation. Facilities should be appropriately constructed and maintained to avoid leaks, flooding, or formation of pockets of moisture in areas where the ammonium nitrate is located.
- Employees should be regularly trained and tested on critical safety procedures and periodic monitoring should take place to ensure that procedures have been followed.

The follow-up investigation also recommended that temperature monitors should be installed in each storage silo.

Case 3

An explosion occurred in an NP buffer in the neutralization process of the production activity. Production in the fertilizer plant had been stopped due to maintenance work in the ammonia storage area, and as a result, there could be no supply of ammonia to the plant. Just prior to the explosion, an automatic fire detector directly connected to the control room of the local emergency preparedness unit and the plant went off. In addition, gas was observed by the operators in the factory and the building was evacuated with staff directed to the designated meeting points. Shortly after the evacuation, the explosion took place. The pressure from the explosion caused window damage in the meeting place area and five operators were injured due to glass fragments. The explosion caused a fire in the third floor of the building. The fire was extinguished after approximately one hour.

The cause of the accident was identified as decomposition of ammonium nitrate in the NP buffer tank due to high temperature and low pH in the tank. These conditions resulted in the formation of a large amount of gas leading to the rupture of the tank from overpressure. The overheating was the result of a leaking steam valve on the 20 bar steam supply to the tank. The NP buffer tank was the last unit before the liquor was pumped to the evaporation and prilling section for making the final product prills. The off gas from the tank is connected to the recovery system for ammonia. In this process, the addition of ammonia neutralizes the acidic liquor from the process immediately beforehand.

The ammonia flow was controlled by an online automatic pH measurement, located at the 25% level of the tank. In addition, ammonium nitrate is added to obtain the correct ratio between N and P in the final product. The NP buffer tank had no instrumented safety functions, but a high temperature alarm on 145°C was installed. Also, there was a high and low alarm on the automatic pH measurement and a high alarm on the online chlorine analyser. Two evenings before the accident a high temperature alarm went off. This was acknowledged and dismissed without investigation. The evening before the accident, the temperature continued to register on the high side, but since the pH was high and the steam valves were shut, it was assumed that the temperature measurement was wrong.

Lessons learned

- No hazards had been associated with the NP buffer tank in the Hazop study or the risk analysis. Hazard identification should have drawn attention to the elevated risk associated with the presence of ammonium nitrate in a process tank while the process was idle. Safety procedures and controls for process equipment are usually designed to manage risks when the process is running and cannot be automatically assumed to be capable of also controlling substances safely in abnormal situations.
- Hazard identification should pay particular attention to the sensitivity of ammonium nitrate to changes in operating conditions. As such it should also take into account the plant life cycle and unintended events that could adversely affect these conditions in order to establish appropriate safety controls and procedures for these situations.
- The installation of appropriate instrumented safety functions is a typical control measure that could assist the operator in limiting consequences from unexpected ammonium nitrate reactions under a wide range of conditions.
- Alarm management is a common challenge at many

(Foto: Reuters/NTB scanpix)

West, Texas explosion 2013

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processing plants where there are numerous processes with numerous alarms for each covering a wide range of functions. The failure to respond to the high temperature alarm suggests that the company did not have an adequate system for prioritising alarms to ensure an appropriate and timely response to emergencies. In addition, employee training should also instil a heightened awareness in operations staff to nonconformities, negative indicators, and pre-emergency alerts during shutdown periods.

Conclusions

The cases described in this paper represent some examples of major accidents involving ammonium nitrate fertilizers, and the lessons derived from these events could contribute to improvements in handling ammonium nitrate fertilizers. The unique safety challenges associated with ammonium nitrate coupled with poor safety management culture could largely be considered as the most important contributing factors across the accidents studied. Insufficient fire prevention, protection and control systems were also common in these accidents. One of the biggest problems in these cases was the lack of knowledge of the inherent hazards associated with the handling and storage of ammonium nitrate fertilizers. Also, the lack of knowledge on the possible decomposition of fertilizers led to major accidents. A key lesson from the case studies, therefore, is the importance of establishing adequate safety procedures in particular relating to training and awareness of hazards.

Furthermore, authorities are responsible for intervening to address land-use planning concerns around ammonium nitrate installations.

Finally, lessons learned from past major accidents that have occurred in their own countries as well as around the world could be beneficial for operators to recognise gaps in the safety management system.

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