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Methodologies for Industrial Accidents Analysis: Key Parameters.

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Science, my lad, is made up of mistakes, but they are mistakes which it is useful to make, because they lead little by little to the truth.

Jules Gabriel Verne

En primer lugar, quiero agradecer a mi tutor, Jaume Giménez Farreras, por la dedicación y sus conocimientos brindados para realizar este proyecto, que me han servido para guiarme durante todas las etapas del mismo, así como la orientación y atención a mis consultas a lo largo del procedimiento. Además del apoyo y el respeto a mis sugerencias para este trabajo desde el primer momento.

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Contenido

SUMMARY

This project establishes a methodology to identify the key factors influencing the initiation and development of a major accident with ammonium nitrate.

Initially, the study shows a detailed analysis of the behavior of ammonium nitrate its mixtures, evaluating the physicochemical factors that influence its properties and the conditions that could lead to this substance to a major accident. This first step includes all situations that involve a dangerous evolution of the properties of ammonium nitrate.

Next step is to collect information of industrial accidents with ammonium nitrate, carrying out a data processing and an appropriate screening of the information to facilitate the order and selection of useful data for this project.

The number of accidents should be sufficiently representative to include in the study all the different outcomes that can occur in a major accident (fire, explosion, leakage and domino effect).

Subsequently, a categorization of the collected accidents has been made according to the damages caused, the substances involved and their quantities. Then a statistical analysis of the categorization of the accidents is made to look for possible patterns leading to a serious accident.

The next step is the selection of four of the thirty-six accidents collected to be analyzed in depth and related to the statistics previously elaborated. Based on this comparison, the most influential key factors in the course of a serious accident are identified.

Finally, the lessons learned in these specific cases are specified, and which are also applicable to the rest of the accidents included in the project.

Key words: Major hazards, Industrial accidents, Ammonium nitrate, Major accidents parameters, Chemical accidents consequences.

RESUM

En el presente proyecto se ha cubierto una primera etapa en orden a establecer una metodología para identificar los factores clave que influyen en los accidentes graves con productos químicos.

En primer lugar, se ha hecho un pequeño resumen de los tipos de riesgos en la industria química y de cómo ha ido evolucionando la seguridad y la legislación relacionadas con las plantas químicas

Para acotar el tema y centrar la aplicación de la metodología, el trabajo se ha basado en accidentes relacionados con nitrato de amonio, aunque la metodología seguida podría ser aplicable para cualquier otro producto químico. Se ha hecho un análisis detallado sobre el comportamiento del nitrato de amonio y las mezclas que forma, evaluando los factores fisicoquímicos que influyen en sus propiedades y las condiciones que puedan llevar a dicha sustancia hacia una situación que pueda desembocar en un accidente grave.

Se ha recopilado información sobre accidentes industriales con nitrato de amonio realizando un tratamiento de los datos y una criba adecuada de la información para facilitar el orden y la selección de los datos útiles para el presente proyecto. El número de accidentes debe ser suficientemente representativo como para que se incluyan en el estudio todos los diferentes desenlaces que pueden darse en un accidente grave (incendio, explosión, fuga y efecto dominó) y también distintas causas.

Posteriormente se ha realizado una categorización de los accidentes recopilados en función de los daños causados, las sustancias implicadas y sus cantidades. Posteriormente, se ha procedido a un análisis estadístico de la categorización de los accidentes para buscar los posibles patrones que conducen a un accidente grave.

Finalmente se han seleccionado cuatro de los treinta y seis accidentes recopilados para analizarlos en profundidad y relacionarlos con las estadísticas elaboradas anteriormente. A partir de tal comparación se ha procedido a identificar los factores clave más influyentes en el desarrollo de los accidentes. Finalmente, como debe hacerse siempre en el análisis de accidentes, se han extraído una serie de lecciones que pueden servir para intentar evitar esos accidentes en el futuro.

Palabras clave: Peligros graves, Accidentes industriales, Nitrato de amonio, Parámetros de accidentes graves, Consecuencias de accidentes químicos.

1. INTRODUCTION

The present project is aimed to study the different types of industrial accidents with ammonium nitrate in the last 100 years, establishing a methodology to identify the key factors for the accidents progress. To achieve the goals, information has been compiled, from scientific sources, on occurred accidents in the past. This information has been classified and structured, allowing a better understanding of the causes, progress and consequences of accidents.

The industrial safety development is analyzed, especially concerning the ammonium nitrate industry, keeping track of its evolution throughout history to understand its current state. This is how we get to know the ammonium nitrate industry has been such a challenge, in terms of safety, for every company all over the years.

1.1 RISK: DEFINITION AND TYPES

Risk can be defined as:

$$R\ (risk)\ =\ P\ (probability)\ x\ S\ (severity)$$

In other words, it is the combination of the probability of a dangerous event and the severity of the damage that such an event could cause.

The risk has several types of classifications, according to different parameters and objectives. Below are three of the different risk classifications [1], which allow better targeting the type of risk analyzed in this study.

Classification according to the application of reduction measures:

- Pure risk: no control measures have been applied.
- Residual risk: measures have been applied to reduce or mitigate the risk.
- Acceptable risk: risk has been reduced or mitigated in such a way that it can be tolerated, taking into account the legal requirements of each country and the occupational safety and health policy. This would be the objective for the chemical industry.

Classification according to the level of avoidance and acceptance:

- Category A risks: they are unavoidable and accepted, without compensation (dying from lightning).
- Category B risks: they are avoidable in principle but must be considered unavoidable if one wants to be fully integrated into modern society (e.g., dying in a car accident). This is where the chemical industry comes in.
- Category C risks: generally avoidable, voluntary and with compensation (e.g., dying in a hazardous sport).

Classification according to industrial activity:

- Conventional risks: related to the existing activity and equipment in any sector (falls, blows, electrocution, etc.).
- Specific risks: related to the handling or use of products that, due to their nature, can cause damage (toxic, radioactive, corrosive products, etc.).
- Major risks: related to accidents and exceptional situations. Their consequences can be particularly serious as the rapid release of dangerous products or energy could affect considerable areas. This is the case of major accidents in the chemical industry: fires, explosions and leaks.

Conventional risks and specific risks correspond to the classic treatment of health and safety at work and are relatively easy to foresee. Otherwise, major risks are a special case, since their effect goes beyond the facilities of a chemical plant, as they can have effects outside the plant, causing irreversible and unpredictable damage to people, environment and properties.

The present project is based on the latter type of risk, which represents too high a percentage of industrial accidents today. It is important to know the difference between risk and danger in order to clearly establish the role of safety, as will be discussed in the following section.

Danger is that which can cause an accident or damage. On the other hand, risk is associated with the probability that a hazard will become an accident with certain consequences (that can cause potential damage). For example, if flammable products are stored in a plant, the danger is in the flammability and this cannot be avoided. However, the application of the correct measures (inertization, tanks fitted with sprinklers and foamers, etc.), reduces the probability of an accident and its consequences and therefore the level of risk is lowered.

1.2 INDUSTRIAL SAFETY AND EVOLUTION

For many years now, there has been great concern for the safety of people during the development of industrial activities. For this reason, the authorities have been repeatedly called upon to establish laws to ensure that work can be carried out without endangering life. The background of history of industrial safety and its evolution (involving ammonium nitrate) explained along this section has been obtained from the documents referenced in [2], [3].

The Hammurabi Code (2100 BC), based on Talion law, is one of the oldest sets of laws that include references to industrial safety [4]. The Hammurabi Code lists laws that promote the welfare of society and refers to the rights of slaves, death and injury in the labor sector (agriculture, livestock and others).

Plato and Aristotle also addressed the issue of occupational health in their time, raising the need for prevention.

Later, in Roman times [5], several specifications were developed for the construction of bridges, roads, aqueducts, etc., increasing workers' safety. During this period, the toxicity of mercury was discovered, according to Pliny and Galen, and the effects of lead on mine workers were determined. This led to the proposal of measures on the health and protection of workers.

Moving forward in time, during the 13th century the Ordinances of France appear, which watches over the safety of the working class, and in Germany a document is written that points out some professional illnesses. This was the first document that dealt with safety and was one of the first texts on occupational health.

Over the years until the 18th century, several studies were published that dealt with issues related to mining, mentioning conditions in the eyes, lungs, joints and poisoning. In addition to mining activity, the safety and illnesses of sailors, soldiers, lawyers and artisans also came into play.

When the Industrial Revolution arrives (18th century), with the appearance of new risks related to the technological development, the need to implement regulations to avoid the frequent accidents in the industry arises. They were first implemented in the most developed countries such as Germany, United Kingdom and the United States, and later in other countries.

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During the 19th century, emphasis began to be placed on the protection of workers from labor accidents, making a defense of the avoidance of bodily injury at work. This is how industrial safety was born. In 1833, the first government inspections were carried out and the "Factories Act" (England) was enacted, considering the health and safety of workers. In 1850, certain improvements were made with regard to protection, ventilation, lighting and other aspects related to health in the work environment.

The formalization of industrial safety came with the publication, in 1931, of the book "Prevention of Labor Accidents" by Herbert William Heinrich, who carried out several studies and analyses of accidents proposing that, within a preventive approach, out of every 100 accidents, 98 can be foreseen. There began, then, to be a certain awareness of industrial safety and it began to be given the importance it required at a global level. In 1970 a proposal by William Steiger on Occupational Safety and Health in the United States is approved, which leads to the creation of the OSHA (Occupational, Safety and Health Administration). From there, similar bodies are created in many countries.

The regulations and studies carried out have been revised and extended until today, giving rise to the current Industrial Safety regulations.

1.3 CHEMICAL INDUSTRY AND MAJOR HAZARDS

Over the years, industrial accidents have occurred with serious effects on people, environment and property. Some examples include Flixborough in 1974, the Seveso plant disaster in 1976, followed by Union Carbide's Bhopal disaster in 1984 and Piper Alpha in 1988, which resulted in deaths and serious property losses.

These disasters highlighted the need to pay special attention to these accidents because of the enormous impact they can have, especially on people's lives, inside and outside of the plant.

These accidents, traditionally known as major accidents, are beginning to be called serious accidents and have exposed the risks raised by the proximity of certain industrial establishments to residential areas, areas frequented by the public and other areas considered of special interest and sensitivity.

Especially since the accident in Seveso (Italy, 1976), society has become increasingly concerned about these accidents and has called on governments to ensure adequate separation between urban areas and establishments presenting such hazards. This led to the creation of the so-called Seveso regulation in the European Union, which focuses on reducing the risks associated with major accidents involving hazardous substances. This implies the requirement of compliance with legislation to ensure strict safety conditions, which is a significant advance in the prevention and protection against major accidents. This legislation implies the protection not only of human lives, which is the most important thing, but also of the environment and property.

Seveso's regulations have evolved in line with technological and industrial advances and the better understanding of the hazardous nature of substances. These regulations have been developed at a European level through Directives, the latest version, known as SEVESO III, has been translated into Directive 2012/18/EU, transposed into Spanish legislation by Royal Decree 840/2015. Likewise, the criteria included in RD 1196/2003 (Basic Directive on serious accidents) are still in force [6].

Royal Decree 840/2015, therefore, refers to the control of the risks inherent in serious accidents involving dangerous substances. This Royal Decree aims at the prevention of this type of accidents, as well as the limitation of their consequences on human health, property and the environment, in accordance with Seveso's regulations. This Royal Decree requires companies to carry out a risk analysis that involves the detection of existing dangers at the plant, accidents that may originate from them, the evaluation of possible consequences and the assessment of risk to people, the environment and property.

These studies allow the determination of intervention and alert zones, which mark the distances of affectation of the possible accidents and within which there cannot be population nuclei. Companies must also draw up plans for self-protection (internal emergency) and must participate in drawing up external emergency plans, which are the responsibility of the Autonomous Communities.

All of this takes the form of a safety report that must be sent to the administration for analysis and approval, if it is the case. This information must be updated periodically and whenever substantial changes have occurred [7].

1.4 AMMONIUM NITRATE

Ammonium nitrate (NH_4NO_3) is not found as a substance in nature. In 1659, the German chemist Johann Rudolf Glauber synthesized it for the first time and called it "Nitram Flammans".

1.4.1 Chemical Properties

- It is a stable compound in its pure form, as it can be kept unaltered at ordinary temperature and pressure.
- When it is in contact with impurities, it is not considered so stable as it becomes particularly sensitive to changes in humidity, pressure, temperature or composition.
- In the presence of salts can easily give double decomposition reactions, in particular, in the presence of alkaline salts, it quickly releases its ammonia.
- It is a strong oxidizing agent that can react and cause violent explosions in the presence of organic matter, certain metals, reducing materials, fuels, acids, sulphur, phosphorus, etc. Like all oxidants, it "improves" the combustion properties of other materials. This can manifest itself in a decrease in the temperature required for a material to burn and an increase in the speed of combustion and the temperature of the materials.
- It is explosive and self-detonating in the absence of water or the application of heat or fire.

1.4.2 Physical Properties

Under normal conditions, i.e., ambient temperature and atmospheric pressure, ammonium nitrate is found in solid state (salt) and it is white to colorless and odorless.

The next table summarizes the physical properties of ammonium nitrate [8], [9].

Table 1: Physical properties of Ammonium Nitrate

Melting Point	169ºC (thermal decomposition)
Bulk density	0.93 – 0.99 g/cm^3
Boiling point	210ºC
Decomposition point	
Density	1.7 g/cm^3
Molecular weight	80.0 g/mole of AN
Granulometry	2 - 4 mm
Solubility (at 20ºC)	192.3 kg of AN can be dissolved in 100 L of water
Hygroscopicity	at 20ºC = 33.1; at 30ºC = 40.6; at 40ºC = 47.5

1.4.3 Industry of Ammonium Nitrate: Production, Storage, Applications and Hazards

Ammonium nitrate (AN) is produced on a large scale worldwide and more than a third of this production takes place in Europe. It is produced by a reaction of ammonia and nitric acid, an irreversible, instantaneous and exothermic reaction. The heat of reaction depends on the concentration of nitric acid used and the solution produced from ammonium nitrate (the higher the concentration of HNO_3, the higher the heat of reaction). The heat produced in the reaction is used to promote the evaporation of the water from the solution.

The process of obtaining ammonium nitrate is divided into four stages:

[1] Neutralization of NH_3 with HNO_3, whose concentration is 55-65%.

[2] Evaporation of water from the resulting solution.

[3] Control of the size of the particles in the crystallization and the characteristics of the dry product, since it is a salt.

[4] When it is to be used as a fertilizer, the final product is coated with a conditioning agent, normally clay, to avoid caking.

Ammonium nitrate is typically supplied in granular form which can vary in purity, size and density. A protective coating is also applied to the lumps to prevent water absorption. Because of the large quantities in which ammonium nitrate is produced, it is commonly stored in silos, piles and sacks. When handling it, it is important to maintain adequate ventilation to avoid undesirable conditions of pressure, temperature and/or humidity, which can be dangerous.

The storage of ammonium nitrate is an important issue that requires considerable attention since, as will be seen in the following sections, it has been a key factor in the industrial accidents that have occurred with this substance. Facilities where ammonium nitrate is stored or circulated should be away from combustible substances, reducing substances and heat sources. Lamps near the ammonium nitrate storage and use area should be protected by a PPF system. The suitable material for containers storing ammonium nitrate is austenitic stainless steel to protect them from corrosion and physical damage.

When ammonium nitrate is stored in solution (normally 10%), the pH must be kept at 4.5 and if it decreases, ammonia gas must be added to bring it back to the appropriate pH value.

It is important to control this variable, especially when working at high temperatures. As a pH higher than 4.5 implies a different composition than the one desired, the new mixture can show an explosion risk [10]. For both storage and transport, ammonium nitrate is classified as an oxidizing agent. When it is a pure product, it can be stored under ambient conditions in large quantities without self-ignition or spontaneous explosion.

The main use of ammonium nitrate is as an agricultural fertilizer. It is an easily absorbed source of nitrogen, efficient for plants and particularly suitable for European climate conditions. Its efficient absorption rate means that it is relatively environmentally friendly compared to other manufactured fertilizers, and the amount of nitrogen lost to the atmosphere is normally low. Among inorganic fertilizers, ammonium nitrate is the most universally used due to its unique combination of bound nitrogen as nitrate and ammonium ions, which are the only two ways plants can efficiently absorb nitrogen from the soil.

Ammonium nitrate, like many other compounds, is usually mixed with other substances to modify certain properties or to achieve specific characteristics of the final product. Thus, in addition to being used as a fertilizer, ammonium nitrate is also the main base material in low-cost and effective blasting agents when properly mixed with carbonaceous materials as fuel. By definition, a blasting agent is any material or mixture formed by a fuel and an oxidizer intended for blasting, provided that the final product cannot be detonated by a blasting cap when it is not confined. It is relevant to note that it was not used in explosives until World War I, when weapons manufacturers mixed it with TNT (or dynamite) to create cheaper bombs. This substance, previously treated, is ANFO (Ammonium Nitrate Fuel Oil), which is used to produce the explosive for civil use in mines, public works and quarries.

On the other hand, if instead of being emulsified, the ammonium nitrate is mixed with mineral oil it can decompose along a lower energy pathway than pure ammonium nitrate. Mineral oil is the only hydrocarbon capable of destabilizing ammonium nitrate.

Ammonium nitrate, in addition to its use in fertilizers and explosives, has an important and wide use in the manufacture of nitrous oxide, an absorbent of nitrogen oxides, an ingredient in freezing mixtures, an oxidant in solid rocket propellants, a nutrient for antibiotics and yeast, and as a catalyst.

If ammonium nitrate is not kept in proper conditions, it can lead to decomposition reactions that can cause explosions, fires and toxic gas leaks. In fact, ammonium nitrate has been involved in serious accidents that have caused many deaths and property damage.

For all these reasons it has been decided to carry out this work focused on accidents with ammonium nitrate, trying to analyze their causes and development and looking for a structured way to study and classify them.

2. OBJECTIVES

The global objective of the project is to establish a methodology to identify the key factors in a major accident in the chemical industry. This work is the first step of the project and will be focused on the accidents related to ammonium nitrate. The achievement of the objective implies next specific objectives:

- The knowledge of ammonium nitrate properties and work conditions related to the possibility of major accidents (fire, explosion, leakage and emission of toxic substances and domino effect).
- The data gathering and processing of industrial accidents with ammonium nitrate.
- The categorization of the different accidents selected according to the damage they caused, the conditions in the moment of the accident, the substances involved and their quantities.
- An in-depth study on four specific accidents, applying the categorization previously established and identifying the key factors and lessons learned.

3. METHODOLOGY

This section shows the detailed methodology applied during this project to obtain the key factors that determine the development of a major accident.

3.1 DATA COMPILATION

This project has required the compilation of a large amount of data from an extensive bibliographical search. During the execution of the project, different types of databases have been used, mainly about industrial accidents, legislation and chemical safety. The types of searched and consulted documents have been articles, reports, studies, data sheets, forums, web pages, books, scientific journals, newsletters and certain newspaper articles.

3.1.1. Database

The databases have been a helpful and useful tool for the analysis of past accidents. The information collected has been systematically structured to include the different types of accidents that can be produced by ammonium nitrate, the different types of reactions involved and the consequences of those accidents, both in human lives and in economic cost.

The main databases used for this project are:

- FACTS. A database which contains approximately 15,000 records on industrial accidents with hazardous substances since 1980. FACTS is related to other sources such as CSB and ARIA.
- eMARS (Minerva). A European database about accidents involving dangerous substances that includes reports on each of them.
- CSB. A database with references of 3000 accidents of transport and storage that involve dangerous substances. It also includes other resources such as images and videos explaining each event that occurred.

- HSE. Official website of the Health and Safety Executive (Great Britain), with data on safety in the chemical industry that includes reports of investigations on industrial accidents.
- OSHA. Official website of the Occupational Safety and Health Administration, with data about accidents and health at work in the USA.
- ARIA. A database with information about investigations on the causes of accidents, the substances involved on it and the process conditions and failures that occurred.
- AIChE. Official website of the American Institute of Chemical Engineers, with data about chemical substances and current events in the chemical industry, including magazine articles, books and blogs.

3.1.2. Research Method

The first step has been the compilation of a massive quantity of generic information, searching with keywords such as "accidents", "ammonium nitrate" or "industrial safety". Once the databases and web pages suitable for this study have been identified, the next stage was to make an advanced research looking for more specific vocabulary.

After making the generic research and the primary specific investigation, about 45 accidents have been found in the industrial field related to ammonium nitrate. The accidents which had enough available information have been selected. In total, 36 accidents were introduced into the study. All of them occurred mainly in ammonium nitrate production and storage plants, although there are also cases of transport or particular facilities.

Once the selection of accidents on which the project is based was done, numerous specific searches were carried out for each of them according to particular aspects such as the industrial sector, geographical area, date of the accident, substances involved, consequences, etc. These searches have been more complex, especially when investigating older accidents. The most common difficulties have been finding out which chemical legislation applied in a given year in a particular country, the amount of ammonium nitrate involved in each accident and the causes of the accidents. For this reason, it has been necessary to compare information from different sources and databases to include only enough contrasted information in the project.

Databases have used to find accidents with ammonium nitrate that have occurred throughout history by filling the main fields such as Accident date (from - , to -), Event type, Industry type, Legislation (Seveso I, Seveso II, Seveso III, UN/ECE, etc.) and Keywords.

Keywords are a fundamental parameter for tracking information. Some of the keywords used in the searches for this study are listed below.

- Ammonium nitrate major hazards
- Ammonium nitrate Explosion
- Ammonium nitrate Accident
- Ammonium nitrate Fire and explosion
- Decomposition of ammonium nitrate
- Ammonium nitrate safety
- Ammonium nitrate disaster
- Ammonium nitrate domino effects
- Chemical Industry Legislation

The advantage of using databases, such as those mentioned above, is that the results found can be sorted according to the date of the event, the type of accident, the type of industry, etc. This helps the research for a specific accident to be much faster.

After the compilation of information, an analysis of dangerous conditions that led to the selected accidents has been carried out, identifying the risk factors of a facility (storage, environmental conditions, operation procedures, etc.) that could trigger a serious accident. The next step was to estimate the possible consequences derived from a hazardous event and the risk associated with specific ammonium nitrate conditions.

The following section shows the detailed analysis of dangerous conditions mentioned.

3.2 CONDITIONS AND CONSEQUENCES OF DECOMPOSITION PROCESSES OF AMMONIUM NITRATE

Ammonium nitrate is sensitive to changes in physical factors (temperature, pressure, etc.) and chemical factors (composition, additives, catalysts, etc.). It is important to know the conditions in which it is found in order to identify which factors can cause the beginning of one or several reactions, which are the reactions that can occur or which changes cause certain conditions on ammonium nitrate and its properties. All this is basic to predict how the reactions end and what consequences they lead to (fire, explosion, leakage, etc.).

Then, the decomposition process is described and the physicochemical factors involved are analyzed, which are closely related and linked them according to the dependency between them. The relations of dependency that exist between them are detailed, as well as the types of accidents that could be triggered: explosion and fire. For the purposes of this project, it is considered that the factors affecting the sensitivity of ammonium nitrate are those that contribute to its deflagration, heating or the reduction of the energy necessary to cause its detonation.

The thermal decomposition process of ammonium nitrate occurs when its properties are disturbed, and it can decompose slowly without exploding or it can have faster and more exothermic decomposition reactions that lead to explosions. Decomposition reactions involve the oxidation of ammonia to nitrogen and water. The by-products generated are oxidizing agents such as O_2 and N_2O, among other nitrogen oxides. The first step in the decomposition mechanism of pure ammonium nitrate is the endothermic dissociation into nitric acid and ammonia. Then, a series of exothermic reactions can take place, which are detailed in Table 2 [11]

As shown in Table 2, the reactions of the thermal decomposition process of ammonium nitrate take place in different temperature ranges. From 80ºC to 100ºC (Equation 1), ammonium nitrate is stable because it is still far from its melting point. In this temperature range, if the heat source is removed, the temperature of the ammonium nitrate drops quickly and the decomposition process would not start.

Table 2: Thermal decomposition of Ammonium Nitrate

Thermal Decomposition Equation	Temperature Range [ºC]	ΔH [kJ/mole of AN]	Equation nº
$NH_4NO_3(s) \rightarrow HNO_3(g) + NH_3(g)$	>100	186	1
$NH_4NO_3(s\ or\ l) \rightarrow N_2O(g) + 2H_2O(g)$	180-200	-37	2
$2NH_4NO_3(s) \rightarrow 2N_2(g) + 2O_2(g) + 4H_2O(g)$	-	-118	3
$2NH_4NO_3(s) \rightarrow 2NO(g) + 2N_2(g) + 6H_2O(g)$	200-230	-	4
$3NH_4NO_3(s) \rightarrow 2N_2(g) + N_2O_3(g) + 6H_2O(g)$	-	-	5
$4NH_4NO_3(s) \rightarrow 2NO_2(g) + 3N_2(g) + 8H_2O(g)$	-	-	6
$5NH_4NO_3(s) \rightarrow 2HNO_3(g) + 4N_2(g) + 9H_2O(g)$	-	-	7
$8NH_4NO_3(s) \rightarrow 2NO_2(g) + 5N_2(g) + 16H_2O(g) + 4NO(g)$	260-300	-	8
$4NH_4NO_3(s) \rightarrow 2NH_3(g) + 3NO_2(g) + NO(g) + N_2(g) + 5H_2O(g)$	260-300	-	9

The pressure is another key factor when studying the detonation conditions for ammonium nitrate. The increase in pressure is generally due to the gases produced by the reaction. The higher the pressure, the higher the temperature and therefore the faster the reaction.

Between 140ºC and 180ºC, the addition of acids, chlorides and chromates, among other materials, contributes to the increase in the reaction speed of ammonium nitrate decomposition. In other words, corrosive compounds significantly increase the sensitivity of ammonium nitrate.

Two cases of addition of catalysts in this temperature range are explained below:

- **Dichromate** is a catalyst that increases the speed of this reaction, modifies the products obtained and increases exothermicity regarding to non-catalyzed reactions.
- **Chlorides** are particularly effective in accelerating the rate of decomposition, since a small amount of chlorides is capable of causing decomposition at temperatures as low as 140 ºC in the presence of free acids. For example, when catalysed with 1% NaCl, the rate of decomposition at 175°C is 1000 times higher than that of pure ammonium nitrate. The acidity of the solution has a strong influence on the sensitivity of ammonium nitrate, since increasing the acidity promotes the decomposition mechanism.

Between 180ºC and 200ºC detonation starts (Equation 2) and is completed according to the reaction of Equation 3, in which the gas generated can reach temperatures of 1500ºC and pressures of approximately 11 bar.

In the range of 200ºC to 380ºC ammonium nitrate shows two modes of decomposition [12]:

- For all temperatures, the first step is the endothermic dissociation into ammonia and nitric acid (reaction a in Table 3).
- Between 200ºC and 290ºC takes place the formation of NO_2^+, whose rate of formation limits the whole process (see reactions b, c and d in Table 3).

Table 3: Decomposition reactions of Ammonium Nitrate in the range of 200ºC to 290ºC

(a)	$NH_4NO_3 \underset{-X}{\Leftrightarrow} NH_3 + HNO_3$
(b)	$HNO_3 + HX \underset{slow}{\Longleftrightarrow} H_2ONO_2^+ \rightarrow NO_2^+ + H_2O$ $HX = NH_4^+, H_3O^+, HNO_3$
(c)	$NO_2^+ + NH_3 \rightarrow NH_3NO_2^+$
(d)	$NH_3NO_2^+ \rightarrow N_2O + H_3O^+$ $NH_4NO_3 \Leftrightarrow N_2O + 2H_2O$

Between 190ºC and 230ºC, the temperature is high enough to initiate a self-sustained decomposition in mixtures of ammonium nitrate with other substances, such as when it is mixed with phosphates.

If the mixture contains copper, iron or other metals, the self-sustained decomposition can be catalyzed causing the exothermic reaction to continue even after the fire is extinguished.

In particular, the mixture of ammonium nitrate with copper is a dangerous combination in fire scenarios as it promotes detonation. In this case, copper nitrate ($Cu(NO_3)_2$) is formed, which decomposes in the presence of heat, promoting a quick exothermic oxidation of metals that normally would not easily react with molten ammonium nitrate, but in this case they do, leading them to explosive conditions.

Above 290ºC, predominates the decomposition through free radicals (see Table 4), giving rise to the process of homolysis of nitric acid that forms nitrogen dioxide and hydroxyl radical, as the determining stage of the speed of the reaction.

Table 4: Decomposition reactions of Ammonium Nitrate above 290ºC

(a)	$NH_4NO_3 \underset{slow}{\Longleftrightarrow} NH_3 + HNO_3$
(b)	$HNO_3 \rightarrow NO_2 + HO\cdot$
(c)	$HO\cdot + NH_3 \rightarrow \cdot NH_2 + H_2O$
(d)	$NO_2 + \cdot NH_2 \rightarrow NH_2NO_2$
(e)	$NH_2NO_2 \rightarrow N_2O + H_2O$

The main gaseous products of the reactions are N_2O and NO_2, and the main by-product is N_2. At 230ºC there is 25% N_2, while at 340ºC the N_2 content is 6% [12]

An increase of temperature accelerates ammonium nitrate decomposition and an explosion can occur if a critical mass or the critical ventilation rate of the area is reached. The critical speed is the air velocity (rate) which is high enough to prevent the "*backlayer*" phenomenon, which consists of the smoke moving in the opposite direction to the ventilation, due to the increasing pressure caused by the temperature in the fire zone. These events favor the conditions of self-acceleration of the reaction in case of fire.

As the rate of decomposition increases, the release of toxic gases (nitrous oxide) that feed the combustion is favored. If the concentration of these substances exceeds 200 ppm, their effects can be fatal even if the exposures are short.

The composition of commercial ammonium nitrate can have a decisive influence on its to decomposition reactions. This composition varies according to its use and can be defined from the degree of purity, the stabilizers, the additives and the moisture content. According to the American Chemical Society (ACS), the degree of ammonium nitrate can be pure, technical, industrial, explosive or fertilizer. The grade specifies the purity, size, composition and moisture content of the ammonium nitrate mixture before it is supplied (to a distributor/seller), i.e. before a secondary mixture is made for specific applications. Generally, additives are materials introduced into the ammonium nitrate mix, such as stabilizers for manufacturing or transportation purposes, to prevent the main substance from accumulating in the process equipment and to provide a moisture barrier against excessive water absorption.

The addition of substances acts on the sensitivity of ammonium nitrate and the energy released in the decomposition reactions. For example, increasing the amount of activated carbon in granulated ammonium nitrate decreases TNT_{eq}, while for powdered ammonium nitrate, increasing the amount of activated carbon increases TNT_{eq}. The $TNT_{equivalent}$ is the quantity of TNT whose explosion releases the same energy as the explosion of a given ammonium nitrate mixture, and which corresponds to the maximum energy production. Above this amount, the release of energy is reduced.

The addition of organic compounds, as in the case of FGAN (0.5% to 1.0% wax-coated ammonium nitrate), contributes to the release of energy in the decomposition reaction and thus increases the hazard. This substance helps the ammonium nitrate mixture to heat up spontaneously and can cause a fire, because adding a fuel (organic compound) to a strong oxidant (ammonium nitrate) promotes combustion.

The composition of the mixture also influences the intensity of the explosion. Thus, if the mixture contains 50% NH_4NO_3, the intensity of the explosion will be relatively small, while if the proportion of NH_4NO_3 is increased to 55-60%, the intensity of the explosion and the explosive properties of the mixture are greatly increased. The detonation of such a mixture is powerful enough to initiate a detonation in a surrounding mixture of a lower NO_3 concentration, which would normally be considered as minimally explosive.

For ammonium nitrate to explode, it must be sufficiently energized for the self-decomposition reactions to take place, and from that point, to have a self-decomposition exothermic reaction there must be enough energy accumulated for an explosion to occur. The start of the process can be of thermal or mechanical origin.

In the first case, it may be due to an external fire that heats the ammonium nitrate mass until it reaches the temperature at which the auto-decomposition reactions begin. This mechanism was the one that occurred in the accidents in Texas City, Brest, Tianjin and Beirut (Table *6*). In the second case, a nearby explosion can provide enough energy for the self-decomposition of ammonium nitrate to take place. Some examples which show this mechanism would be the accidents at Kriewald, Oppau, Tessenderlo and Traskwood (see Table *6*). In this second case, the process is generally much faster due to the notably higher amount of energy that reaches the ammonium nitrate mass at the beginning.

In both cases, adequate containment conditions must be provided so that the accumulation of vapours, generated by self-destruction, can reach the necessary pressure for the explosion to occur. Therefore, in open spaces or storage conditions with a lot of free space, it will be much more difficult for the explosion to occur.

The speed of detonation is directly related to the amount of energy released in an explosion and is used as an indicator. In other words, the higher the speed of detonation, the greater the energy production. When ammonium nitrate is fully detonated it produces an energy release of approximately 400 cal/g, which corresponds to a 40% of the energy released by TNT (1120 cal/g) in its detonation. Otherwise, ammonium nitrate does not represent a serious hazard in relation to dust explosion, as pure oxidants can even serve as inert agents to inhibit the explosion.

The above-mentioned mechanisms for the detonation of ammonium nitrate could correspond to a situation of domino effect, in which a fire reaches a quantity of ammonium nitrate, causing it to self-decompose and subsequently explode. The primary scenario is fire and the secondary scenario is detonation. The domino effect is the combination of effects that multiplies the consequences of a dangerous event in such a way that it can affect, in addition, to the exterior vulnerable elements, other containers, pipes or equipment in the same establishment or in other nearby establishments, causing a new leak, fire, explosion of containers, which in turn causes new dangerous phenomena [13]. For a domino effect occurrence, a first accident must occur that reaches nearby facilities, but it does not necessarily have to be a serious accident. This particular sequence of events is common to several of the accidents compiled in the following sections.

In confined areas of an industrial facility there is a higher risk of a domino effect due to the little separation between equipment, piping and instrumentation. Ammonium nitrate is usually stored in enclosed spaces in the form of piles in order to protect it from external impurities and moisture. This condition has advantages and disadvantages since, in terms of industrial safety, a confined space is an area where there is a potential risk of serious accident. Confinement has interdependent relationships with temperature and pressure: depending on the level of confinement, an increase in temperature also implies an increase in pressure, especially in spaces with poor ventilation.

It has been commented that ammonium nitrate is stored in piles in confined places and this implies a risk of explosion, which is also related to the particle diameter, since, depending on this, the self-decomposition reactions of ammonium nitrate can occur at greater or lesser speed. The size of the particles has a notable influence on the sensitivity (stability and self-decomposition) of ammonium nitrate since, as the size of the particles is reduced, the sensitivity of the substance increases, although its influence contributes less than that due to the presence of contaminants and/or humidity. Under ambient conditions (atmospheric pressure and ambient temperature) and without confinement, pure ammonium nitrate has a very low sensitivity, regardless of particle size.

Apart from the risk of explosion, an accident with ammonium nitrate can only result in a fire. Pure ammonium nitrate fires are less intense and more manageable, while ammonium nitrate fires mixed with organic matter are more intense and extensive, sometimes involving transition to explosion. Two fire mechanisms could be described for ammonium nitrate and its organic mixtures [11].

- **Mechanism A:** The fire is generated by an external heat source that affects the surface of the ammonium nitrate mass. If the installation is ventilated and the effect of large gas accumulation does not occur, large quantities of ammonium nitrate can be consumed without an explosion. This is also related to the fact that, in this case, the decomposition process of ammonium nitrate takes place in a specific area on the surface of the material, which makes the reaction slower, the temperatures not as high and the pressure increase lower, preventing detonation. Examples of this mechanism would be the accidents at Muscle Shoals, Gibbstown, St. Stephens and Presque Isle (see Table 6).

- **Mechanism B:** The fire can occur by self-heating of ammonium nitrate, especially when stored in large quantities. This self-heating can trigger self-decomposition reactions, the process of which is usually slow, allowing control if it is detected and acted upon quickly enough. This process is accelerated in the presence of catalysts or organic material. In several cases of fire, large amounts of ammonium nitrate have been involved and have been burned or extinguished without further incident. This shows that the amount of ammonium nitrate is not only a determining factor in the severity of the possible accident, but also relates to the particular circumstances in which the self-destructive reactions have occurred.

Table 5 summarizes the variations in sensitivity of ammonium nitrate and energy release as a function of the parameters explained above.

Table 5: Variations of Sensitivity and Energy output with different parameters.

Increasing Factor	Sensitivity	Energy Output
Particle Size	↑	↓
Organic Contaminant	↑	↑
Inorganic Contaminant	↓	↑
Metal/Chloride Contaminant	↑	↑
pH	↑	-
Confinement	↑	-
Temperature	↑	↓
Pressure	↑	-

↑ Increasing Effect
↓ Decreasing Effect
- No Effect

3.3 DATA CATEGORIZATION

This section shows the categorization of the data obtained from the selected accidents, quantifying the following parameters: type of accident, products involved, amount of ammonium nitrate involved and human damages, reflected in the number of deaths and injuries per accident. It is observed that in several cases different substances are involved, in addition to ammonium nitrate. In some cases, the amount of substance involved in the accident is unknown due to the paucity of information on the accident.

All this is summarized in Table 6, where the selected accidents are indicated in chronological order. Each accident has been listed and from now on they will be mentioned and referenced by their number.

On the other hand, the economic impact caused by this type of accident is detailed, as well as the environmental damage caused. These last two have been evaluated in a qualitative and quantitative way.

Table 6: Major Accidents involving Ammonium Nitrate

Nº	Location	Date	Type	Substance	Amount [tonnes]	Fatalities	Injuries	References
1	Gibsstown, New Jersey (USA)	15/05/1916	Explosion	AN	1.81	14	12	[1], [14]
2	Faversham, Kent (UK)	02/04/1916	Explosion	AN + TNT	700 (AN) + 25 (TNT)	115	0	[15] [16]
3	Oakdale, Pennsylvania (USA)	15/09/1916	Explosion	AN + TNT + TNA	1.4	6	8	[17], [18], [19]
4	Kriewald (Poland)	26/07/1921	Explosion	AN + water + inorganic contaminants	30	19	0	[20]
5	Oppau (Germany)	21/09/1921	Explosion	AN + Ammonium Sulfate	450	600	2000	[21], [22], [23]
6	Nixon, Nova Jersey (USA)	01/03/1924	Fire + Explosion	AN	2	18	15	[24]
7	Muscle Shoals, Alabama (USA)	04/04/1925	Fire + Explosion	AN	-	0	0	[14]
8	Miramas (France)	05/08/1940	Fire + Explosion	AN	240	0	0	[20]
9	Tessenderlo (Bèlgica)	29/04/1942	Explosion	AN	150	189	909	[20]
10	Texas City (USA)	16/04/1947	Fire + Explosion	AN + AS	2086 (AN) + 870 (AS)	581	3000	[25], [26], [27]
11	Brest (France)	28/07/1947	Fire + Explosion	AN	3310	29	0	[28], [29], [20]
12	Presque Isle, Maine (USA)	26/08/1947	Explosion	AN	240	0	0	[30], [14]
13	St. Stephen, New Brunswick (Canada)	1947	Fire	AN	400	0	0	[14]
14	Red Sea	23/01/1953	Fire + Explosion	AN	3600	0	0	[31]
15	Roseburg, Oregon (USA)	07/08/1959	Fire + Explosion	AN + TNT	4.5	14	125	[32], [33]
16	Traskwood, Arkansas (USA)	17/12/1960	Toxic Emission	AN Fertilizer + Fuel	160	0	0	[7]
17	Taroom, Queensland (Australia)	30/08/1972	Explosion	AN	12	3	0	[34]
18	Kansas City, Missouri (USA)	29/11/1988	Fire + Explosion	AN + ANFO	23	6	0	[35], [36]
19	Porgera Gold Mining (Papua New Guinea)	02/08/1994	Fire + Explosion	ANE	80	11	0	[31]
20	Port Neal (USA)	13/12/1994	Explosion + Toxic Emission	AN + HNO_3 + NA vapour	70	4	18	[37] [38]
21	Denmark	24/09/1996	Toxic emission	AN	3.,8	1	6	[39]
22	Xingping, Shaanxi (China)	06/01/1998	Explosion	AN	27.6	22	56	[40]

Nº	Location	Date	Type	Substance	Amount [tonnes]	Fatalities	Injuries	References
23	Toulouse (France)	21/09/2001	Explosion	AN	400	31	2500	[10], [27]
24	Cartagena, Múrcia (Spain)	26/01/2003	Fire	AN	-	0	0	[41]
25	Saint-Romain-en-Jarez (France)	02/10/2003	Fire + Explosion	AN	4	0	26	[42], [20]
26	Mihalesti, Buzau (Romania)	24/05/2004	Fire + Explosion	AN	20	18	3	[43], [44]
27	Ryongchon (North Corea)	22/04/2004	Explosion	AN	40	162	3000	[20]
28	Estaca de bares (Spain)	19/02/2007	Fire + Toxic Emission	AN	394	0	0	[1], [45]
29	Monclova, Coahuila (Mexico)	09/09/2007	Fire + Explosion	AN	222	28	150	[46]
30	Porsgrunn (Norway)	03/12/2008	Fire + Explosion	AN	-	0	0	[47]
31	Bryan, Texas (USA)	30/07/2009	Fire	AN + NH_3	-	0	-	[20]
32	West, Texas (USA)	17/04/2013	Fire + Explosion	AN	240	15	200	[48], [11], [27]
33	Wyandra, Queensland (Australia)	05/09/2014	Explosion	AN	56	0	7	[23], [49], [46]
34	Finland	2015	Leak + Toxic Emission	AN	-	0	0	[50]
35	Tianjin (China)	12/08/2015	Fire + Explosion	AN	800	173	797	[51] [52], [20]
36	Beirut (Lebanon)	04/08/2020	Explosion	AN	2750	+200	+600	[53], [54]

Table 6 shows the main information of the thirty-six (36) accidents included in the study of this project, from which statistics have been obtained in relation to the type of accident, the substance involved, the number of deaths and number of injuries, which are represented and discussed below.

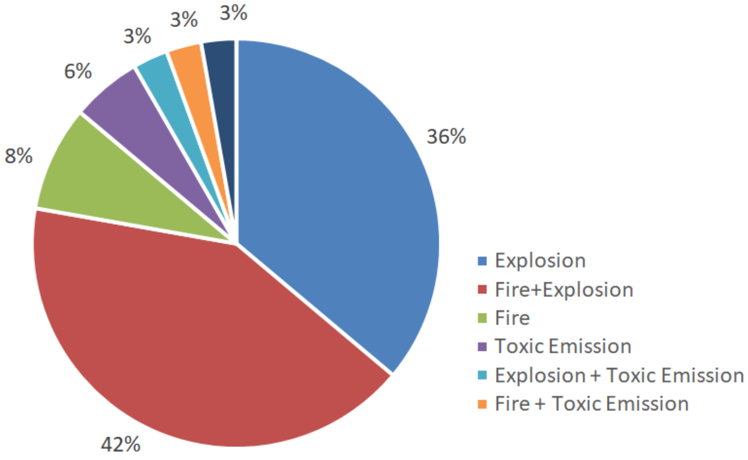


Figure 1: Distribution according to the type of accidents involving Ammonium Nitrate

According to the distribution represented in Figure 1, the types of accidents studied are:

- **Explosion.** This event involves the sudden release of energy, which generates an overpressure wave that moves away from the epicentre of the explosion while dissipating energy. The release of this energy must be sufficiently fast and intense so that the wave that is generated is perceptible. According to the graph of the distribution of the types of accidents studied (Figure 1), 81% involve the phenomenon of explosion, taking into account the cases of explosion only, those of fire + explosion and those of explosion + emission of toxics. The scenario of explosion is the accident that occurs most often.
- **Fire.** Among the various accidents that can occur in the industry, this type of event is the one that, in general terms, has a smaller affectation radius. That is, it takes place in a more localized manner and that makes it easier to control if it is detected early enough so that the thermal radiation does not affect other parts of the plant and generate new accidents (leaks or explosions). On the other hand, smoke can complicate the intervention of specialized teams involved in such accidents and subject them to an additional danger (lack of visibility or poisoning).

As shown in Figure 1, the fire scenario includes fire, fire + explosion and fire + emission of toxics. All of them represent 53% of the accidents studied.

- **Toxic emission.** This event also includes a massive number of accidents, taking into account that, most of the times that a fire or an explosion occurs, there is a gas or liquid leak somewhere in the installation. Mainly it is the emission of ammonia, gases derived from nitrogen (NO_2, N_2O, etc.) or combustion gases. There can also be emissions of liquid materials that are usually corrosive, polluting and dangerous, affecting human health, the environment and the installation itself. Figure 1 shows the cases of toxic emissions that have posed a serious danger in terms of human and environmental damage, and which account for 12% of the cases studied, considering the emission of toxic only and the emission of toxic due to a fire and explosion. However, it can be considered that for the rest of the fire and explosion accidents there has also been toxic emission, in some extent.

According to the substances involved in the accidents studied, two groups have been differentiated, as shown in Figure 2: accidents in the presence of ammonium nitrate and accidents in the presence of a mixture with ammonium nitrate:

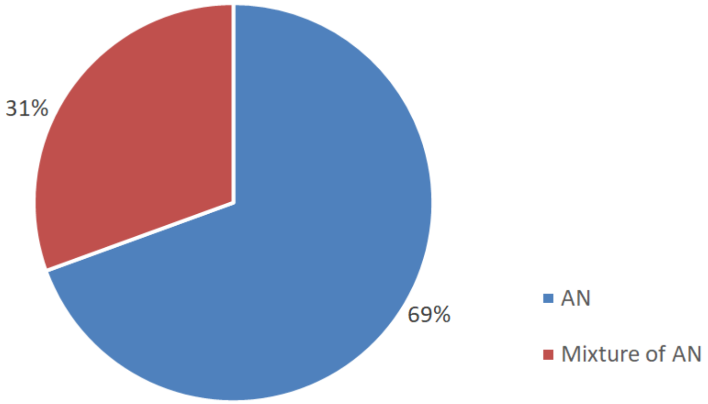


Figure 2: Distribution according to the substances involved

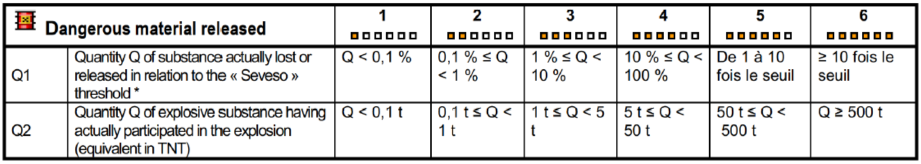
The substance involved in 69% of the cases was ammonium nitrate, either pure or with a very low percentage of additives (<5%). In the remaining accidents, which represent 31% of the cases studied, more than one substance other than ammonium nitrate has been involved, such as TNT, HNO_3, NH_3, ANE, ANFO, etc. (see Table 6). In many cases, ammonium nitrate is the one produced in a fertilizer plant, which implies that the substance involved was a fertilizer, which has ammonium nitrate as its main component.

The European Scale of Industrial Accidents (1994) [55] establishes criteria for evaluating accidents based on 18 parameters according to the following groups of effects and consequences:

- Two parameters concern the quantities of hazardous substances involved
- Seven bear parameters on the human and social aspects
- Five parameters concern the environmental consequences
- Four parameters concerning the economic aspects

Each of these 18 parameters include six levels. The highest level determines the accident's index. Table 7, Table 8, Table 9 and Table 10 show the criteria of the European Scale followed to evaluate the consequences of the four accidents studied in the next Section.

Table 7: Dangerous material released Criteria



Dangerous material released		1 ■□□□□□	2 ■■□□□□	3 ■■■□□□	4 ■■■■□□	5 ■■■■■□	6 ■■■■■■
Q1	Quantity Q of substance actually lost or released in relation to the « Seveso » threshold *	Q < 0,1 %	0,1 % ≤ Q < 1 %	1 % ≤ Q < 10 %	10 % ≤ Q < 100 %	De 1 à 10 fois le seuil	≥ 10 fois le seuil
Q2	Quantity Q of explosive substance having actually participated in the explosion (equivalent in TNT)	Q < 0,1 t	0,1 t ≤ Q < 1 t	1 t ≤ Q < 5 t	5 t ≤ Q < 50 t	50 t ≤ Q < 500 t	Q ≥ 500 t

* Use the higher "Seveso" thresholds. If more than one substance are involved, the higher level should be adopted.

The Figure 3 shows the relation between human damage to the amount of ammonium nitrate involved in each accident, involving those accidents for which there was enough available data.

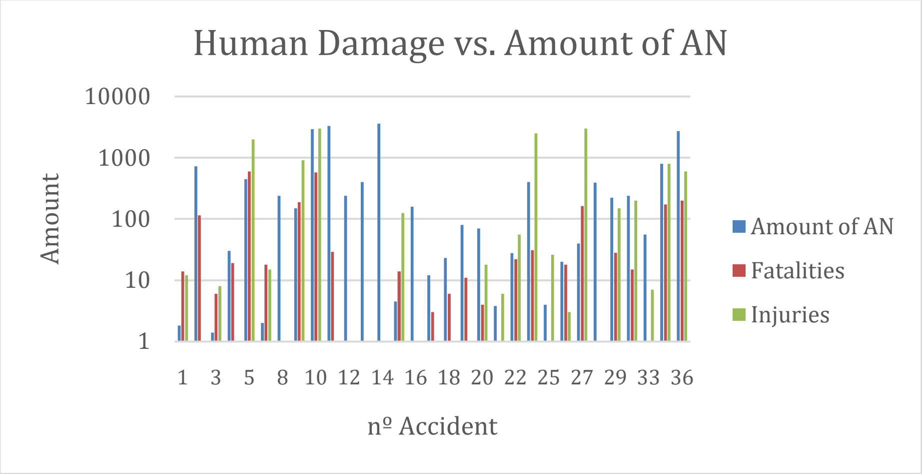


Figure 3: Human Damage vs. Amount of AN in different accidents

It is right that the amount of NH_4NO_3 involved in an accident can influence on damage, but, as can be seen in Figure 3, the number of deaths and injuries has no an apparent direct relation to the amount of ammonia and the substances involved in the accident (Figure 2 does not show any trend according to these variables).

The reason for all this is that the severity of an accident is related to other variables, in addition to the amount of substance involved. These include:

- The distance between the population and the plant, as well as the number of people working in the facility and its surroundings at the time of the accident.
- The physicochemical conditions of the substance since they determine whether the event is more violent/intense or not.
- The time it takes to detect the effect of radiation, overpressure or concentration of toxics. It is clear that the more time passes and the longer it takes to apply the measures and activate the emergency plan, the more serious the consequences may be. For example, if a fire is detected in time, its expansion can be prevented, and it cannot cause another serious accident by domino effect.

Table 8: Human and social consequences Criteria

Human and social consequences		**1** 🟥□□□□□	**2** 🟥🟥□□□□	**3** 🟥🟥🟥□□□	**4** 🟥🟥🟥🟥□□	**5** 🟥🟥🟥🟥🟥□	**6** 🟥🟥🟥🟥🟥🟥
H3	Total number of death: including - employees - external rescue personnel - persons from the public	- - - -	1 1 - -	2 – 5 2 – 5 1 -	6 – 19 6 – 19 2 – 5 1	20 – 49 20 – 49 6 – 19 2 – 5	≥ 50 ≥ 50 ≥ 20 ≥ 6
H4	Total number of injured with hospitalisation ≥ 24 h: including - employees - external rescue personnel - persons from the public	1 1 1 -	2 – 5 2 – 5 2 – 5 -	6 – 19 6 – 19 6 – 19 1 – 5	20 – 49 20 – 49 20 – 49 6 – 19	50 – 199 50 – 199 50 – 199 20 – 49	≥ 200 ≥ 200 ≥ 200 ≥ 50
H5	Total number of slightly injured cared for on site with hospitalisation < 24 h : including - employees - external rescue personnel - persons from the public	1 – 5 1 – 5 1 – 5 -	6 – 19 6 – 19 6 – 19 1 – 5	20 – 49 20 – 49 20 – 49 6 – 19	50 – 199 50 – 199 50 – 199 20 – 49	200 – 999 200 – 999 200 – 999 50 – 199	≥ 1000 ≥ 1000 ≥ 1000 ≥ 200
H6	Total number of homeless or unable to work (outbuildings and work tools damaged)	-	1 – 5	6 – 19	20 – 99	100 – 499	≥ 500
H7	Number N of residents evacuated or confined in their home > 2 hours x nbr of hours (persons x hours)	-	N < 500	500 ≤ N < 5 000	5 000 ≤ N < 50 000	50 000 ≤ N < 500 000	N ≥ 500 000
H8	Number N of persons without drinking water, electricity, gas, telephone, public transports > 2 hours x nbr of hours (persons x hours)	-	N < 1 000	1 000 ≤ N < 10 000	10 000 ≤ N < 100 000	100 000 ≤ N < 1 million	N ≥ 1 million
H9	Number N of persons having undergone extended medical supervision (≥ 3 months after the accident)	-	N < 10	10 ≤ N < 50	50 ≤ N < 200	200 ≤ N < 1 000	N ≥ 1 000

3.3.1. Environmental Damage

The damage caused to the environment can be due to spills of polluting products into surrounding waters, leaks of toxic substances into the ground and groundwater, emissions of toxics into the atmosphere, the reach of radiation and flames from a fire or the overpressure from an explosion.

The damage caused by these events leads to the death of the species of flora and fauna present at the time of the accident, either through poisoning, the impact of overpressure or the effect of the flame of a fire, in addition to the effect on the soil and surrounding water. In some cases, the damage caused can be alleviated with time and human labor, but in many cases it is irreversible. For example, the accident at the AZF factory (Toulouse, 2001) resulted in a spill of nitrogen compounds into the Garonne River that killed hundreds of species in the area's ecosystem.

Current environmental legislation generally imposes limits and conditions to prevent this impact from exceeding certain levels considered to be tolerable [55].

Table 9: Enviromental consequences Criteria

Environmental consequences		1 ■□□□□□	2 ■■□□□□	3 ■■■□□□	4 ■■■■□□	5 ■■■■■□	6 ■■■■■■
Env10	Quantity of wild animals killed, injured or rendered unfit for human consumption (t)	$Q < 0,1$	$0,1 \le Q < 1$	$1 \le Q < 10$	$10 \le Q < 50$	$50 \le Q < 200$	$Q \ge 200$
Env11	Proportion P of rare or protected animal or vegetal species destroyed (or eliminated by biotope damage) in the zone of the accident	$P < 0,1$ %	$0,1\% \le P < 0,5\%$	$0,5\% \le P < 2\%$	$2\% \le P < 10\%$	$10\% \le P < 50\%$	$P \ge 50\%$
Env12	Volume V of water polluted (in m^3) *	$V < 1000$	$1000 \le V < 10\,000$	$10\,000 \le V < 0.1$	0.1 Million $\le V <$ 1 Million	1 Million $\le V <$ 10 Million	$V \ge$ 10 Million
Env13	Surface area S of soil or underground water surface requiring cleaning or specific decontamination (in ha)	$0,1 \le S < 0,5$	$0,5 \le S < 2$	$2 \le S < 10$	$10 \le S < 50$	$50 \le S < 200$	$S \ge 200$
Env14	Length L of water channel requiring cleaning or specific decontamination (in km)	$0,1 \le L < 0,5$	$0,5 \le L < 2$	$2 \le L < 10$	$10 \le L < 50$	$50 \le L < 200$	$L \ge 200$

* The volume is determined with the expression Q/C_{lim} where:

- ✓ Q is the quantity of substance released,
- ✓ C_{lim} is the maximal admissible concentration in the milieu concerned fixed by the European directives in effect.

3.3.2. Economical Impact

The economic impact of an accident will, of course, depend on the type and amount of substance involved and also, as indicated above, on the particular conditions under which the accident has occurred. When estimating the cost of an accident, it is necessary to take into account not only those direct costs that are perfectly observable but also those indirect costs that arise as a consequence of the accident.

In this respect and in a similar manner, Simonds [56] talks about insured and uninsured costs. It is clear that costs are not exactly the same for all accidents, but the concepts included in each group are very illustrative of all the costs that can arise as a result of an accident. We also consider the above mentioned about costs that could sometimes go unnoticed.

Insured costs are those covered by the insurance company. On the one hand, they cover damages to persons, including medical costs, compensation to persons affected by loss of salary, temporary or permanent disabilities, costs for compensation to relatives and funeral expenses. The insurance company also covers costs for loss of equipment, facilities and product (up to the insured amounts), compensation for use and occupation, etc. [55].

Uninsured costs are those that the company must assume and include different damages. Firstly, they include production costs that are not covered by the insurance company, such as cost differences of lost products, inactive machinery, equipment rentals, etc. They also cover costs related to the injured, such as first aid, transport, medical services, etc.

Part of labor costs must also be covered by the company. In addition, the company must cover the costs of lost wages (reparations, cleaning and replacements caused by the accident). Costs such as investigations and reports on the event can also be important. In the case of serious accidents (especially with fatalities), costs related to lawsuits and legal issues must be taken into account. Furthermore, fatalities or injuries of the workers imply a loss of skill and experience, decreased production due to replacements, decreased cooperation of the staff, etc. In this way, four types of accidents are taken into account when estimating these costs using the Simonds Method:

- Accidents that generate lost working days due to absence from work.
- Accidents that require medical assistance but do not result in absence from work.
- Accidents requiring first aid and no absence from work.
- Accidents that do not cause any injury.

The economic consequences are divided into six levels, according to the Table 10 below:

Table 10: Economic consequences Criteria

€ **Economic consequences**		**1** ■□□□□□	**2** ■■□□□□	**3** ■■■□□□	**4** ■■■■□□	**5** ■■■■■□	**6** ■■■■■■
€15	Property damage in the establishment (C expressed in millions of € - Reference 93)	0,1 ≤ C < 0,5	0,5 ≤ C < 2	2 ≤ C< 10	10 ≤ C< 50	50 ≤ C < 200	C ≥ 200
€16	The establishment 's production losses (C expressed in millions of € - Reference 93)	0,1 ≤ C < 0,5	0,5 ≤ C < 2	2 ≤ C< 10	10 ≤ C< 50	50 ≤ C < 200	C ≥ 200
€17	Property damage or production losses outside the establishment (C expressed in millions of € - Reference 93)	-	0,05 < C < 0,1	0,1 ≤ C < 0,5	0,5 ≤ C < 2	2 ≤ C < 10	C ≥ 10
€18	Cost of cleaning, decontamination, rehabilitation of the environment (C expressed in millions of € - Reference 93)	0,01 ≤ C < 0,05	0,05 ≤ C < 0,2	0,2 ≤ C < 1	1 ≤ C < 5	5 ≤ C < 20	C ≥ 20

4. IN-DEPTH STUDY OF FOUR ACCIDENTS

This section shows four major accidents selected from the thirty-six studied in 3.3. The first part exposes an extension of the development of each accident and their characteristics to evaluate the key factors that determined the ending of each case.

Likewise, the concepts of environmental damage, human damage and economic impact explained above are related to each accident and the future lessons learned in each case are presented.

4.1 SELECTED MAJOR ACCIDENTS

The four major accidents selected are:

- Oppau, 1921. Explosion (disaggregation related).
- Texas City, 1947. Fire and explosion (transport related).
- Port Neal, 1994. Explosion and toxic emission (process related).
- Toulouse, 2001. Explosion (storage related).

It has been decided to do a deeper research into these accidents since they have several different causes and many of them are very similar to the ones that cause other accidents in Table 6. Hence, the key factors identified through the study of these accidents in this section will be representative and applicable to most of the major accidents included in this project.

Moreover, the development and outcome of each of them are very different and involve different conditions and circumstances, which allow studying ammonium nitrate in a very wide range of circumstances.

4.1.1. Oppau, Germany Accident

On September 21st, 1921, took place an accident at a chemical plant in Oppau, Germany [57]. The source of the accident was a warehouse where 4500 tons of ammonium nitrate were stored and used to produce fertilizers.

Previously, in 1919, several production tests had been carried out to check the explosiveness of the mixture being treated at the plant, which concluded that sulphate and ammonium nitrate mixtures with less than 60% ammonium nitrate were not explosive, therefore this fertilizer was treated as a non-hazardous material.

Later, in 1921, the process was modified by increasing the humidity level from 2% to 3-4% and consequently decreasing the density. Then, no further tests were carried out on the new fertilizer obtained, which was a 50:50 mixture of ammonium nitrate and ammonium sulfate, whose explosive properties were:

- In case of explosion with confined conditions and with a relatively low density, the event is limited to the area around which the explosives are placed.
- Certain physical properties of the fertilizer (density, humidity, etc.) have a big influence on its ability to explode.
- The increase of the ammonium nitrate concentration from 50 to 60% in a mixture contributes to the significant increase of the explosiveness and the explosive power of such a mixture. Through the investigations that were carried out later, it was possible to determine that the mixture had an ammonium nitrate concentration between 47 and 49%.

This mixture was heterogeneous, which means that some parts that were more enriched in ammonium nitrate than others. In terms of stability, the mixture was not stable, also because the mass was not uniform. This fact implied a change in the properties of the final product, significantly increasing its sensitivity to external conditions.

The day of the event, dynamite was used to disaggregate the mixture, as a standard procedure that had been carried out several times without incident. However, in this case, it was not this way, as the impact occurred against an area that contained a mixture of 55-60% ammonium nitrate that caused the explosion of the mixture, causing the detonation of another adjacent 50:50 mixture. Although only 10% of the main mixture was detonated (450 tons of 4500), the explosion was heard over 275 km and caused a domino effect that caused multiple fires in all plant facilities, resulting in other minor explosions.

The accident was a major disaster in terms of human damage. In total, there were 600 dead, 2000 injured and more than 7,500 homeless people.

Material damage was also severe: the chemical plant building was completely destroyed, creating a crater almost 11,000 m^2 (90 m x 120 m) in area and 20 m deep. In addition, all nearby boats on the Rhine River were damaged, the surrounding telecommunications facilities were destroyed, and several homes were severely damaged.

According to an article in the New York Times of January 29th, 1922, the material damage was evaluated at $1,700,000.

The implementation of the emergency plan was delayed because there was a danger of further explosions through domino effect, so that all emergency services (doctors, firemen, ambulances, French and German Red Cross volunteers, army, etc.) could not act until after several hours.

4.1.2. Texas City, USA Accident

The accident occurred on April 16th, 1947 in Texas (USA) and involved two cargo ships (Grandcamp and High Flyer) [58]. The events took place in Texas City, a seaport that included a large industrial complex of warehouses, chemical plants and refinery [59], [60].

On the morning of April 16th, the cargo ship Grandcamp, docked in the port of Texas City, was loaded with about 2,300 tons of ammonium nitrate fertilizer. The crew detected smoke in the cargo area. In order to keep the cargo intact, it was decided not to use water to extinguish the fire but rather to use an extinguisher to put out the flames, although the operation was not successful. Afterwards, they tried to reduce the amount of oxygen by closing the hold and pumping out pressurized steam, but ammonium nitrate does not need oxygen for self-sustaining decomposition. So, the flames continued to spread and the temperature increased within the cargo area until it raised enough to cause a large explosion that was heard up to 150 miles away.

The flames spread until they reached the High Flyer, another cargo ship carrying 1050 tons of sulfur and 960 tons of ammonium nitrate, which also caught fire and exploded. Oil tanker boats near the site burned for days, consuming massive amounts of petroleum.

After several subsequent studies, the cause of the disaster was attributed to a spontaneous heating of the ammonium nitrate.

The consequences in terms of human damage were devastating: 581 people died and 3,000 were injured. People working on the docks died instantly. A nearby chemical storage facility also exploded, killing 234 of the 574 workers, and almost all of the survivors were seriously injured.

The cloud left by the explosion rose to 600 meters in the air, causing two small planes passing overhead to crash. In addition, the explosion triggered a 12-foot tidal wave that destroyed numerous buildings, leaving up to 2,000 people homeless. Incandescent pieces of steel from the facilities that had been destroyed by the explosion fell over a wide radius, starting numerous fires. The crude oil tanks caught fire, and a chain reaction (domino effect) continued to spread the fire to other structures that had not previously been damaged. The next day, large columns of thick black smoke could be seen 50 km away.

The total loss of private property was estimated at approximately $100,000,000, which was divided into compensation for the 1,400 victims, property damage, etc. In addition, there were other additional costs such as the 1.5 million barrels of oil products consumed in flames, valued at about $500,000,000, or the total destruction of Monsanto's plant which represented an estimated cost of $20,000,000.

4.1.3. Port Neal, USA Accident

On December 13th, 1994, an explosion took place at a fertilizer plant in Port Neal, USA. On the day of the accident, production at the plant had stopped due to maintenance work, precisely in the ammonia storage area. For this reason, during the plant shutdown there was no ammonia supply in the entire process chain.

During a procedure to stop the process, compressed air was applied to the nitric acid line inside the neutralizer, followed by pressurized steam at 200 psig and temperatures up to 220ºC [37], where there was a highly acidic and chloride-contaminated solution. These conditions led to the formation of a large amount of gas that caused the tank to rupture due to overpressure and consequently, overheating occurred, which induced the fertilizer to catch fire. This was followed by the detonation of 70 tons of ammonium nitrate solution in the process neutralizer.

The research team determined that metallurgical observations and analysis indicated that a local area within the neutralizer had been exposed to a temperature of 927ºC or more. Several analysis of the neutralizer fragments and the waste tank indicated that the containers were fragmented due to overpressure, indicating that all or part of the contents of the containers may have exploded. Analysis confirmed that both the neutralizer and the waste tank exploded.

There were multiple causes of the accident [37]:

- The day before the disaster an alarm was triggered by the detection of high temperatures, but the situation was dismissed because the pH values were right and the steam valves were closed.
- On the day of the accident the ammonium nitrate decomposed due to the high temperature and low pH of the tank.
- The application of the steam flow in the nitric acid line was too long, causing the steam flow to have very acidic conditions ($pH < 1$). This occurred, partly, because the pH measuring probe was designed to operate at a maximum temperature of 140°C and, as much higher temperatures were reached, it broke down.
- Bubbles were created that generated low density zones in the neutralizer, in addition to a poor cooling flow due to the leakage of cooling water that occurred, making the solution highly sensitive to temperature increases. Air, steam and gas bubbles provided "hot spots" during thermal decomposition or deflagration because the gas they contain is adiabatically compressed by the advance of the pressure wave.
- The currents involved were contaminated with chlorides.
- During the plant shutdown the tanks were full, which always means a risk of overflowing, leaks and, in case of accident, larger quantities of product involved.

During the event there was a large release of decomposition gases due to the fire and the rupture of two tanks caused by the explosion, which caused the leakage of 15,000 tons of ammonium nitrate, HNO_3 and toxic vapors.

The leakage of these substances forced the evacuation of 1,700 residents from the surrounding area. In addition, there was a great environmental impact that destroyed part of the surrounding flora and affected certain species of animals in the area.

The overpressure of the explosion caused damage to the facilities in the area (glass breakage) and a fire in the same building.

The human damage could have been worse, compared to what could have happened. Even so, four people died and 18 were injured.

The economic costs of the accident reached the value of $321,000,000, which covered compensation for the injured people and the families of the dead ones, damage to neighbouring facilities, and environmental damage caused by the accident, especially leaks of toxic substances.

4.1.4. Toulouse AZF Accident

On September 21st, 2001, an explosion occurred at the AZF fertilizer plant in Toulouse, France [10]. The plant was dedicated to the manufacture of nitrogen and industrial nitrate fertilizers and the production of chlorine derivatives.

The events took place in shed 221, where agricultural or industrial ammonium nitrate was manufactured and stored. It was considered "low quality" due to its grain size and chemical composition (not specified). There were about 400 tons stored, separated by partitions. It should be noted that the plant also stored large quantities of other hazardous chemicals such as pressurized ammonia, liquid chlorine, fuel and methyl alcohol.

The establishment fell within the scope of the SEVESO I and SEVESO II Directives; due to the presence of the substances it was treating (ammonia, chlorine, ammonium nitrate, etc.). Since 1982 many studies were carried out (revised and updated every 5 years) of the production process on possible hazards. In these studies, several accident scenarios were analyzed, but the problem of ammonium nitrate detonation was not considered, since there was a specific storage method implemented in the plant.

The day before the disaster, 18 tons of ammonium nitrate with additives were moved to shed 221, and the day of the accident, the amount of 500 kg of DDCNa was added.

The following causes were firstly considered as possible, but later were discarded:

- Intentional external causes (attack, malicious act and missile). From a legal point of view, this hypothesis is not supported by any tangible facts.
- Process incident (electrical failure in the plant, etc.). However, an examination of the manufacturing parameters at the time of the accident did not justify this type of incident.

- Impact of a metal part causing a primary explosion on top of a tower near the site of the explosion. However, experts believe that the kinetic energy developed by the projection of the pieces would be insufficient to explode the nitrate contained in shed 221.

Finally, the causes of the disaster were attributed to a combination of incompatible substances that triggered a violent chemical reaction that resulted in an explosion. Therefore, it was determined that the explosion had been accidentally caused by a mistake in the handling and of products.

The caliber of the explosion was equivalent to an earthquake of magnitude 3.4 on the Richter scale, was perceived up to 75 km away and its intensity is evaluated in the equivalent of 20 to 40 t of TNT. The explosion caused a crater of about 3000 m^2 (65 m x 45 m) and 7 m deep formed in the place of the deposit.

The human damages produced were devastating. In total, 31 people died and 2,500 were injured:

- 21 died at the AZF plant.
- 1 died at the nearby SNPE plant.
- 500 m from the epicenter, a student died and several others were injured when a concrete structure collapsed.
- Two people died, located 380 m and 450 m from the epicenter.
- Thousands of people were hospitalized for serious and minor injuries and many suffered from psychological problems (anxiety, depression, etc.).
- During 2 months, medical tests were carried out on about 6,000 children, located within a radius of 2 km around the site. Five percent of the secondary school children and 6.3 percent of the primary school/kindergarten children were hearing-impaired (> 25 dB).
- NO_2, NH_3 and other toxic particles released by the explosion caused eye and respiratory irritations in the population living near the site.

The plant was completely destroyed. In terms of material damage, the explosion reached all kinds of facilities:

- 1,300 industrial, commercial and artisan companies affected to varying degrees (21,000 employees).
- Within a radius of 3 km, 26,000 homes were damaged.
- The blast wave and various projectiles reached and damaged 120 schools and 3 university residences.
- An appliance store, located 320 m from the epicenter of the explosion, and a vehicle maintenance facility, located 380 m away, collapsed due to the effect of the overpressure.

The damage caused was estimated at between 1,500 and 2,300 million Euros, which includes:

- Soil diggings for treatment and decontamination, which had a cost of 100,000,000.
- The destruction of warehouses around the plant, including one that housed one hundred buses, had a cost of 30.5 million Euros.
- Major material damage and production losses for the plant operator, neighbouring plants, retailers and individuals, including the cost of cleaning and rehabilitation measures in the area, which were worth over 2 billion Euros.

The fire fighting and rescue measures were immediately applied. The authorities and government departments activated the emergency centres; the PPI (special administrative accident response plan) and the plant emergency plan were put in place. Reinforcements had to be requested for all bodies acting at the site of the explosion (firemen, police, doctors, etc.). Disaster and hazardous substances technology specialists carried out the operations of recovery and removal of ammonium nitrate in hot solution, industrial nitrates buried near the crater, liquefied ammonia, nitric acid and other residual substances from the explosion in the area.

In total, more than 750,000 m^3 of soil and other quantities of concrete were excavated for decontamination through on-site washing and heat treatment at 850°C. Nevertheless, the environmental impact was very serious. There had been a spill of about nine tons of ammonia that caused massive pollution along 1.5 km of the Garonne River, killing 8,000 fish and some species of aquatic flora. The soil in the area was heavily contaminated and the entire area of the facility was destroyed due to the crater left by the explosion and the leakage of toxic substances.

4.2 EVALUATION AND APPLICATION OF CRITERIA. KEY FACTORS

It is quite clear that industrial accidents do not have a single cause, but the final event is usually caused by a series of dangerous situations that lead to a catastrophic outcome.

In this section, the conditions and parameters of the four accidents analyzed in section 3.1 above (Oppau, Texas City, Port Neal and Toulouse) are evaluated according to the concepts set forth in section 1 and section 2:

- The evaluation of the physicochemical conditions that contribute to situations that implies a potential danger of causing a fire and/or explosion scenario. For this stage, the sensitivity of ammonium nitrate to the external changes studied is especially taken into account: temperature, pressure, humidity, confinement, presence of contaminants (organic or inorganic additives), pH, presence of catalysts, etc. (Table 5).
- The evaluation of the damage caused and the economic impact caused according to the European scale of industrial accidents in section 2 [55].

From this point, the key factors that have influenced the cause, development and outcome of each of the accidents can be identified.

Oppau, 1921

The mixture involved was heterogeneous and suffered an increase of humidity to 3-4%, providing instability and contributing the self-decomposition of ammonium nitrate. So, when the impact of the dynamite for the disintegration of the fertilizer took place, the fertilizer exploded.

The fact that the explosion took place in a workshop implies that it was in a sufficiently confined area to favour the increase in pressure, and consequently, increased the sensitivity of the ammonium nitrate mixture.

The explosion caused a domino effect as it reached other plant facilities, causing minor explosions and fires.

The table 11 shows the damage caused by the disaster and its level of severity:

Table 11: Oppau Consequences

Parameter	Description	Level
Dangerous Materials Released	450 tonnes of an ammonium nitrate mixture and ammonia sulphate 50:50	6
Human Damage	600 fatalities and 2000 injuries	6
Enviromental Damage	Destroyed soil and toxic gases emission	0
Economical Impact	Accident Cost between 500.000$ and 200.000.000$	4

Key Factors:

- Uncontrolled composition changes. During the event there was an increase in the proportion of NH_4NO_3 of 55-60% and an increase in humidity, increasing its explosive properties.
- Fertilizer stored in large quantities.

<u>Texas City, 1947</u>

This is a special case in which there was a spontaneous heating of ammonium nitrate, for unknown reasons. However, the crew's response at the time of the event was not the most appropriate. The cargo ship Grandcamp had a very high amount of ammonium nitrate in the hold, a place that is considered a confined area, due to its small dimensions in proportion to the amount of hazardous substance it stored. The confinement of the area (hold) favored a quick increase in temperature and consequently the ignition of the substance was initiated. That means it contributed in a high proportion to increase the sensitivity of ammonium nitrate to changes in external physicochemical conditions.

Due to the fire, the reaction speed increased exponentially until the ammonium nitrate reached a situation of self-heating, which led to its detonation.

The domino effect occurred due to the proximity between cargo ships that stored dangerous substances: oil, ammonium nitrate and sulphur, among others. The explosion at the Grandcamp reached the High Flyer, causing it to catch fire and then explode. This is a clear example of the dangerousness of a domino effect, capable of multiplying the consequences exponentially.

The following table summarizes the damage caused by the accident:

Table 12: Texas City Consequences

Parameter	Description	Level
Dangerous Materials Released	Grandcamp explosion: 2.300 tonnes of ammonium nitrate High Flyer explosion: 1050 tonnes of sulphur and 960 tonnes of ammonium nitrate	6
Human Damage	581 fatalities and 3000 injuries	6
Enviromental Damage	Formation of a cloud of toxic vapours from the combustion of oil and ammonium nitrate	0
Economical Impact	Accident Cost > 200.000.000$	6

Key Factors:

- Poor response from the staff:

  Insufficient ventilation due to the closure of the hold at the beginning of the heating of the mixture

- Highly confined area

Port Neal, 1994

The operating temperature of the neutralizer was 130.5ºC [37]. The decomposition conditions were not yet reached but, as the temperature progressively increased and the pH decreased, the sensitivity of ammonium nitrate raised significantly.

Inside the neutralizer, the pressure increased due to the increase in temperature until the tank broke, which caused the overheating of the fertilizer mixture. The temperature continued to rise until the mixture caught fire. Under these conditions the temperature was already high enough to start the decomposition of the ammonium nitrate and finally to cause its detonation.

The confinement factor contributed to a domino effect. The overpressure from the explosion extended a high temperature atmosphere that caused fires in all plant facilities.

All these physicochemical conditions implied certain unavoidable risks in the process line, such as the formation of bubbles in the neutralizer flow, which provided "hot spots" during thermal decomposition, creating low density zones in the neutralizer. This situation favored the instability of the mixture and its sensitivity to changes in temperature, pressure and pH.

The following table shows a summary of the damage caused according to the European scale of industrial accidents.

Table 13: Port Neal Consequences

Parameter	Description	Level
Dangerous Materials Released	70 tonnes of ammonium nitrate	4
Human Damage	4 fatalities and 18 injuries	3
Enviromental Damage	Release of toxic gases Leak of 15000 tons of ammonium nitrate, HNO_3 and toxic fumes. Destruction of the surrounding flora and affected certain animal species in the area	1
Economical Impact	Accident Cost > 200.000.000$	6

Key Factors:

- Tanks at the limit of their capacity
- Human error:
  - Rejection of high temperature alarm.
  - Application of the steam flow in the nitric acid line during an excessive period of time.
- Uncontrolled effect of pH

Toulouse, 2001

An incompatible mixture of sodium dichloroisocyanurate (DCCNa) and ammonium nitrate was produced, which caused a highly exothermic and violent reaction, producing a rapid increase in the temperature of the mixture. For that reaction, DCCNa acted as a catalyst for the decomposition mechanism of ammonium nitrate [61], which occurred in the melting range of ammonium nitrate. The melting of the ammonium nitrate led to and the decomposition products of DCCNa produce Cl_2, HCl, HNO_3 and large amounts of nitrogen oxides.

The presence of chlorides contributed to the increased sensitivity of ammonium nitrate to its explosive capacity, by raising its decomposition reaction rate.

The secondary reactions significantly affected the generation of heat and its influence on the mixtures. These conditions caused the speed of the ammonium nitrate decomposition reaction to increase so rapidly that detonation and a large release of toxic gases occurred. This fact shows that the presence of inorganic additives increases the sensitivity of ammonium nitrate, increasing its explosive capacity.

There was no domino effect beyond the northern part of the factory, where several tanks containing ammonium nitrate were destroyed and nitric acid leaked. The explosion did not extend to other facilities and chemical plants in this area.

The damages caused by the disaster and the level of its severity are showed below:

Table 14: Toulouse Consequences

Parameter	Description	Level
Dangerous Materials Released	40 tonnes of ammonium nitrate with additives and 500 kg of sodium dichloroisocyanurate	4
Human Damage	31 fatalities and 2500 injuries	6
Enviromental Damage	Destruction and contamination of soil Contamination of Garona river	2
Economical Impact	Accident Cost > 200.000.000$	6

Key Factors:

- Human error:
    - Incorrect manipulation of products. The handling operations were carried out by the staff of a subcontracted company.
- Storage of large quantities of hazardous chemicals
- The hangars containing the ammonium nitrate were adjacent to a building where fuel products were stored.
- There was no fire or nitrogen oxide detection system, although a note was sent to the DRIRE (*Direction Régionale de l'Industrie, de la Recherche et de l'Environnement*) as this improvement was implemented.

4.3 LESSONS LEARNED

Several lessons for the future have been learned and listed based on the evaluation of the Oppau, Texas City, Port Neal and Toulouse accidents, as well as the identification of the respective hazards and key factors detailed in Section 4 above.

Oppau Explosion

i. **Control of changes**. Before modifying part of the process, which involves a change in the properties of the product involved, the process must be tested to ensure that it is safe. After applying the modification, periodic tests and revisions must be carried out. This accident is a clear example of the importance of making revisions to all modifications made, however minor. Since they can lead to a significant increase in the sensitivity of the manufactured product and trigger an explosion.

ii. **Determination of the influence of a change**. When making any change in the process, the effects on the safety characteristics of the materials must be known. This involves knowing the potential hazard of a process in which some parameter has been changed and the failures that may trigger this potential hazard.

iii. **Learning from the past**. Two months before the accident, 19 people died in Kriewald when a wagon containing ammonium nitrate exploded after an explosive was detonated [57]. After this event, safety measures and procedural changes should have been employed to break up the fertilizer by firing dynamite. This case demonstrates the importance of taking into account the experiences of others in similar plants that carry out similar operations, in order to apply the necessary changes and prevent the same accident from occurring.

iv. **Quantity stored**. Avoid the accumulation of product in the same area. It is important to distribute the quantities of product whenever possible, especially when handling hazardous substances such as ammonium nitrate.

Texas City Fire and Explosion

i. **Knowledge of the hazards and actions**. It is essential to know which are the dangers at the workplace and the hazardous materials involved in order to know how to apply the correct procedures in the development of emergency plans in case of an accident. Developing an emergency plan properly has the following advantages:
    a. Hazardous conditions that would aggravate an emergency situation can be discovered and eliminated.
    b. Deficiencies in staff management and coordination can be uncovered: training of staff and workers, adequacy of resources and supplies, etc.
    c. Promote safety awareness and show the organization's commitment to the safety of its workers.
    d. All plant personnel know what actions imply an emergency plan, including evacuating the area, isolating the dangerous scenario and in necessary cases, resorting to external assistance.

ii. **Implementation of safety procedures**. All procedures related to the production, handling and transport of chemicals must be documented

iii. **Identification of scenarios**. In this case, the only scenario that was considered hazardous at the storage facility was the accidental release of anhydrous ammonia [62]. Conducting comprehensive hazard identification and analysis and risk assessment at locations where hazardous substances are stored or handled is a fundamental requirement for the operation of hazardous establishments.

iv. **Separation of materials**. It is advisable to establish a minimum separation between combustible materials and organic substances to reduce the probability of ignition and possible explosion. In this case, cargo ships should have been moored at a greater distance.

v. **Application of measures**. Fire prevention, protection and mitigation measures are essential when working with hazardous substances in bulk. In the case of the

Grandcamp only fire extinguishers were available, which proved to be insufficient for the mitigation of the initial fire.

vi. **Supervision of the activity**. Local authorities and workers involved with such activity should be aware of the dangers involved in handling substances such as ammonium nitrate and supervise their handling. Even if relatively small amounts are involved, the activity can pose significant risks if they are very close to human development.

Port Neal Explosion

i. **Installation Maintenance**. Keep the facilities in good condition to avoid the introduction of impurities in the ammonium nitrate that is treated throughout the process.

ii. **Preventive measures**. Take the necessary measures to prevent birds and animals from coming into contact with the product. If this preventive measure does not work, the ammonium nitrate must be stored in another facility.

iii. **Formation of the employees**. It is a basic requirement to ensure the correct development of the plant, which involves the proper management and control of operations during plant shutdown. In addition to the ability of staff to participate in safety procedures. In the case of the Port Neal accident, employees were dismissive of high temperature alarms, indicating that staff should be made more aware of such alerts during the plant shutdown period. Training for all employees should be conducted on a regular basis. Similarly, follow-up investigations should be made through supervisions every certain period of time and quality monitoring should be carried out.

iv. **Avoid undesired mixtures**. In the storage of ammonium nitrate and its mixtures, contact with water should be avoided to prevent caking, since this physical change can alter its properties and accelerate oxidation. It is therefore important that the installations are properly maintained so that no leaks, flooding or the formation of moisture at the location of the ammonium nitrate occur.

v. **Alarm monitoring**. This task is a challenge for plants where there are many simultaneous processes, which involves controlling many parameters at the same time. If the staff does not consider an alarm of excessive temperature detected, as in this case, it implies that the company probably did not establish an appropriate system to prioritize the alarms. Therefore, the employees didn't achieve an appropriate response.

Toulouse Explosion

i. **Implementation of accident related plans**. City councils should use their land use plans to keep commercial or residential areas away from danger by establishing a safety plan for the neighbourhood community. This was not done during the accident in Toulouse [62].

ii. **Information to the population**. When a chemical plant is located near an urban center, it is important to keep the inhabitants informed about the type of industrial activity that takes place. This facilitates the implementation of external emergency plans and the cooperation of the inhabitants, as they can better understand the situation.

iii. **Update Safety Reports**. It is obligatory to prepare safety reports when handling hazardous substances in a facility and that these reports are reviewed, updated and approved, to ensure safety in the plant. At the AZF factory, the SEVESO II directive was applied, requiring the plant operator to prepare a safety report and send it to the public control authorities, among other tasks. According to company sources, the operator carried out risk analyses, scenarios of possible accidents, etc. However, no document contained a massive ammonium nitrate explosion.

iv. **Employees Formation**. If the work area involves the presence of ammonium nitrate, all employees must have sufficient training and awareness to work in the handling of this substance and, in particular, the danger of ignition. In the case of AZF, the ammonium nitrate storage facilities were managed by subcontractors, whose knowledge of the products and the site was poor.

v. **Process reviews**. Periodic reviews of the operating procedures in the production chain of a chemical facility should be conducted to ensure that they are safe. Such reviews are done through inspections by public control authorities. In the case of AZF, it was an external plant safety management company that had conducted the last inspection in May 2001, four months before the accident.

vi. **Risk Assessment**. The risks of the ammonium nitrate site have to be included within the possible scenarios of major accidents and the domino effects related to dangerous substances stored or produced on the site have to be carried out.

vii. **Quantity of hazardous substances stored**. When different hazardous substances are handled and stored in the same space it is advisable to reduce the amount stored.

5. CONCLUSIONS

Within the general objective of establishing a methodology to identify the key factors of accidents in chemical plants, it has been established, as a first step, a methodology that has made it possible to identify the key factors that influence the origin, development and outcome of a major accident with ammonium nitrate.

The analysis of the accidents studied and of the physical and chemical properties of ammonium nitrate indicates that this product can experience different decomposition reactions, and even self-decomposition, depending on the composition of the mixture in which it is present. These reactions develop at different speeds and can lead to fire or explosion depending, in addition to the composition of the reacting mixture, on the environmental and storage conditions of the ammonium nitrate.

The accidents analyzed show that the consequences for people, the environment and property are very particular in each case and depend on the parameters mentioned above.

The lessons learned from the accidents worked are fundamentally related to safety organization issues that include lack of procedures to lack of emergency plans, deficiencies in the training of workers, failures in performing risk analyses, lack of updating of safety reports, lack of information to the population, change control, lack of maintenance, etc. This deficiency in the organization of safety also extends to material measures such as: quantity of substance stored, separation of incompatible products, deficient ventilation systems, ineffective and/or insufficient means of extinguishing fires, inadequate and/or non-existent alarm systems and other more concrete prevention and protection measures.

As a final conclusion, it could be highlighted that the methodology used has been useful to identify key parameters in ammonium nitrate related accidents

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ACRONYMS

ACS	American Chemical Society
AN	Ammonium Nitrate
ANE	Ammonium Nitrate, fuel and water emulsion
ANFO	Ammonium Nitrate - Fuel Oil
AS	Ammonium Sulphide
AZF	*AZote Fertilisants* (fertilizers plant in Toulouse)
BLEVE	Boiling Liquid Expanding Vapor Explosion
DCCNa	Sodium Dichloroisocyanurate
DDT	Deflagration to Detonation Transition
DRIRE	*Direction Régionale de l'Industrie, de la Recherche et de l'Environnement*
OSHA	Occupational Safety and Health Administration
PFP	Passive Fire Protection
TNA	Trinitroaniline
TNT	Trinitrotoluene
UK	United Kingdom
USA	United States of America
UVCE	Unconfined Vapor Cloud Explosion