UNDERGROUND MINING ENGINEERING 27 (2015) 49-63 UDK 62
UNIVERSITY OF BELGRADE - FACULTY OF MINING AND GEOLOGY YU ISSN 03542904

Review paper

AMMONIUM NITRATE EXPLOSION HAZARDS

OPASNOSTI OD EKSPLOZIJE KOJE POTIČU OD AMONIJUM NITRATA

Negovanović Milanka[1], Kričak Lazar[1], Milanović Stefan[1], Đokić Nikola[1], Simić Nikola[1]

Received: November 18, 2015 **Accepted:** December 10, 2015

Abstract: Ammonium nitrate (AN) primarily is used as a fertilizer but it is also very important compound in the production of industrial explosives. The application of ammonium nitrate in the production of industrial explosives was related with the early era of Nobel dynamite and widely increased with the appearance of blasting agents such as ANFO and Slurry, in the middle of the last Century. Throughout the world millions of tons of ammonium nitrate are produced annually and handled without incident. Although ammonium nitrate generally is used safely, accidental explosions involving AN have high impact resulting in loss of lives and destruction of property. The paper presents the basic properties of ammonium nitrate as well as hazards in handling of ammonium nitrate in order to prevent accidents. Several accidents with explosions of ammonium nitrate resulted in catastrophic consequences are listed in the paper as examples of non-compliance with prescribed procedures.

Key words: ammonium nitrate, explosion, accident, handling, storage, transport

Apstrakt: Amonijum nitrat (AN) primarno se koristi kao đubrivo ali je takođe i veoma važan sastojak u proizvodnji industrijskih eksploziva. Primena amonijum nitrata u proizvodnji industrijskih eksploziva povezana je sa ranim dobom Nobelovih dinamita, a uveliko je povećana sa pojavom eksplozivnih sastava kao što su ANFO i Slari, sredinom prošlog veka. Milioni tona amonijum nitrata se godišnje proizvede i koristi bez incidenata širom sveta. Iako se obično amonijum nitrat bezbedno koristi, nesreće sa eksplozijama u kojima je uključen amonijum nitrat imaju visok uticaj, dovodeći do gubitka života ljudi i uništavanja imovine. U radu su prikazane osnovne karakteristike amonijum nitrata, kao i opasnosti pri rukovanju amonijum nitratom u cilju sprečavanja nesreće. Nekoliko nesreća sa eksplozijama amonijum nitrata koje su dovele do katastrofalnih posledica navedene su u radu kao primer nepoštovanja propisanih procedura.

Ključne reči: amonijum nitrat, eksplozija, nesreća, rukovanje, skladištenje, transport

[1] University of Belgrade – Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia,
e-mails: milanka.negovanovic@rgf.bg.ac.rs; lazar.kricak@rgf.bg.ac.rs; stefan.milanovic@rgf.rs; nikola.djokic92@rgf.rs; nikola.simic1991@rgf.rs

1. INTRODUCTION

Ammonium nitrate (AN) has extensive use in the area of nitrogen fertilizers and explosives (Elvers, 1989; Suslick,1992). AN is the main oxidizing salt in many types of industrial explosives. While the production of dynamite and powder AN/TNT and AN/NG explosives was strictly related to factory production, the production of blasting agents like ANFO, Slurry, emulsion and heavy ANFO approached to the mines as the places of consumption. The production of Slurry and ANFO at mines (on the spot - NALIM system) in Serbia was started in mid 70's of the last Century. The first production of ANFO by the system NALIM was on June 2nd, 1975 while the first filling with Slurry explosives - MAJDANIT was started on October 29th, 1976 in the mines of RTB Bor, Serbia (Kričak et al. 2010).

The next stage in the development of explosives was the invention of emulsion explosives and finally heavy ANFO as a mixture of emulsion and ANFO explosives. Bulk explosives such as ANFO, Slurry and heavy ANFO had the influence on rapid reduction of the production of dynamite and explosive sensitive powder explosives.

Ammonium nitrate has different forms depending upon its use. Ammonium nitrate in crystalline form, porous prills/granules or as saturated aqueous solution is mainly used for the production of industrial explosives. Ammonium Nitrate Based Fertilizers are uniform mixtures in prill or granular form containing ammonium nitrate as the main ingredient.

The application of AN in the production of different types of explosives is presented in Table 1, (Kričak et al. 2010).

Table 1 - Application of AN in the production of different types of explosives (Kričak et al. 2010)

The main oxidizing salt	Component		Explosive	
Ammonium nitrate	+	Trotil	=	Ammonium nitrate powder explosives
	+	Nitro-glycerine	=	Dynamite
	+	Fuel oil	=	ANFO
	+	Water, fuel oil, thickener	=	Water-gel explosives Slurry
	+	Water, fuel oil, emulsifier	=	Emulsion explosives
	+	Emulsion Matrix	=	Heavy ANFO

2. PHYSICAL AND CHEMICAL PROPERTIES OF AMMONIUM NITRATE

Ammonium nitrate is obtained by neutralization of nitric acid with ammonia. It is highly soluble in water and very hygroscopic. Therefore, it should be protected from moisture during storage and transportation.

Ammonium nitrate has a positive oxygen balance +20%. It enables the content of oxygen in excess as compared with the quantity of oxygen required for the oxidization of all the oxidizable compounds present in the explosive or deriving from its decomposition. For this reason, ammonium nitrate is the main oxidizing salt in many types of explosives.

Many properties of AN especially those relevant to its use as a component of explosive mixtures are well documented (Mellor, 1922; US Department of Commerce, 1972; Elvers,1989, Suslick, 1992). Pure ammonium nitrate is very stable and should meet specified quality requirements to be used in the production of industrial explosives. Some of these properties are summarized in Table 2.

Table 2 - Required properties of AN for the production of industrial explosives (Kričak et al. 2010)

Required properties of AN	Values
Molecular weight	80.05
Nitrogen content	34.5%
Ammonia nitrogen	17.25%
Acid nitrogen	17.25%
Melting point	169.6°C
Crystal density	1.725 kg/l
Decomposition temperature	200°C aprox.

Table 3 presents the basic physical and chemical properties of ammonium nitrate with 34.8% N produced by the Company for the production of fertilizers and nitrogen compounds "HIP-AZOTARA" Pančevo (HIP-Azotara, 2015)

Table 3 - Properties of AN 34.8%N produced by the Company "HIP-AZOTARA" Pančevo (HIP-Azotara, 2015)

Properties of AN 34.8% N	Values
Appearance-physical state and color	White solid granules
Odour	Odourless
pH	5.43
Melting point	169.7°C
Initial boiling point and boiling range	169.7°C
Flammability	Not flammable, but may intensify fire
Relative density	1.72 g/cm^3
Solubility	Highly soluble in water >100 g/l
Decomposition temperature	>210°C
Oxidizing properties	Ammonium nitrate is classified as an oxidizing substance
Explosive properties	Not explosive
Miscibility with other substances	Well soluble in pyridine, methanol and liquid ammonia

3. THE MAIN CHEMICAL HAZARDS ASSOCIATED WITH AMMONIUM NITRATE

The main chemical hazards associated with ammonium nitrate are (European Fertilizer Manufacturers' Association, 2000):

- Fire;
- Decomposition;
- Explosion

3.1. Fire

Ammonium nitrate itself does not burn. Being an oxidizing agent, it can facilitate the initiation of a fire and intensify fires in combustible materials. Hot AN solution can initiate a fire in fags, wooden articles etc., on coming into contact with them. Similarly, fertilizer products or dust contaminated with oil or other combustible materials can also start fires when left on hot surfaces (European Fertilizer Manufacturers' Association, 2000).

Fires involving AN cannot be extinguished by the prevention of air ingress because of the provision of oxygen from the AN.

3.1.1. Firefighting Measures

Fire may be caused by non-compliance with the instructions for use or not following the operating instructions (negligence, carelessness, lack of knowledge) (HIP-Azotara, 2015).

In case ammonium nitrate is caught by fire, plenty of water must be used and call the fire brigade. Water is the only known satisfactory extinguishing agent for an ammonium nitrate fire (Canadian Legal Information Institute, 2015). As an ammonium nitrate fire progresses, large quantities of very toxic gases are evolved.

Firefighters must be protected by wearing suitable protective clothing and self-contained breathing apparatus. They must also be trained for carrying and properly using the equipment (HIP-Azotara, 2015).

If the initial fire is not extinguished but progresses, the next step is the evacuation of personnel in the safety distances. There is no possibility either method to predict at what point will explosion occur, but in almost all the explosions of ammonium nitrate affected by the fire there was always enough time for the evacuation (Kričak et al. 2010).

3.2. Decomposition

When pure ammonium nitrate is heated, a slow dissociation to nitric acid and ammonia becomes noticeable at a relatively low temperature, the reaction absorbing heat. At about 93ºC, the solid ammonium nitrate begins to sublime and the rate of sublimation increases until the melting point of 169ºC is reached. The molten material vaporizes at an rate as the temperature is raised (Compressed Gas Association, 1963).

At a temperature of about 210ºC, a reaction begins resulting the formation of nitrous oxide and steam according to the following reaction equation (Kričak et al. 2010):

$$NH_4NO_3 \rightarrow N_2O + 2H_2O + 44.83\text{kJ/mol} \qquad (1)$$

This reaction releases heat and becomes more rapid as the temperature rises.

When the ammonium nitrate is heated rapidly and the temperature allowed to rise to the range of 260ºC to 290ºC, the decomposition increasingly follows the various side reactions in which higher oxides of nitrogen as well as elemental nitrogen and oxygen and steam are formed. These reactions are highly exothermic and rapid, and if the ammonium nitrate and the products of the reaction are confined, so that the temperature or pressure rise cannot be controlled, the reaction may become explosive according to the reaction equation (Kričak et al. 2010):

$$2NH_4NO_3 \rightarrow 2N_2 + 4H_2O + O_2 + 41490\text{kJ/kg} \quad (2)$$

These decomposition reactions refer to pure solid AN. The presence of certain impurities may lower the decomposition temperature. A number of materials have a strong catalytic effect on the thermal decomposition of AN. These include acids, chlorides, organic materials, chromates, dichromates, salts of manganese, copper and nickel and certain metals such as zinc, copper and lead (European Fertilizer Manufacturers′ Association, 2000).

The release of toxic fumes is one of the main hazards associated with the decomposition of AN. Decomposition may produce nitrogen oxides (NO, NO_2, ...), ammonia and amines (HIP-Azotara, 2015). Pure solid ammonium nitrate does not heat spontaneously.

3.3. Explosion

According to EFMA (European Fertilizer Manufacturers′ Association, 2000), AN is especially difficult to detonate and neither flame, spark nor friction is known to cause detonation. Shocks derived from detonating gas mixtures (hydrogen/oxygen or acetylene/oxygen) have been found to be incapable of producing detonation in AN. AN fertilizer dust, being non-combustible in nature, does not give rise to a dust explosion such as those commonly associated with grain and organic dusts. Shock initiation in solid prilled AN needs a fairly substantial stimulus. Heating under confinement and shock initiation of hot or contaminated AN by projectile impact appear to be more credible mechanisms in the context of industrial operations (European Fertilizer Manufacturers′ Association, 2000).

Strongly acidic conditions and the presence of contaminants should be avoided to counter the explosion hazard in AN solutions. Explosions can occur when ammonium nitrate is heated under confinement in pumps (European Fertilizer Manufacturers′ Association, 2000).

4. CLASSIFICATION OF AMMONIUM NITRATE

In Safety Data Sheet of the Serbian Company for the production of fertilizers and nitrogen compounds "HIP - AZOTARA", Pančevo from May 15th, 2015 (HIP-Azotara, 2015) ammonium nitrate 34.8% N is classified according to the Rulebook on classification, packaging, labeling and advertising of the chemical and certain article in accordance with the Globally harmonized system of classification and labeling of the UN ("The Official Gazette of the RS", no.64/10, 26/11, 5/12 and 105/13) as presented in Table 4.

As can be seen in Table 4, ammonium nitrate is classified as oxidizer which may intensify the fire. AN is not self-ignitable, however it can burn even in the absence of air. When heated it melts and may cause decomposition and release of toxic gases containing nitrogen oxides and ammonia. In the presence of reducing agents ammonium nitrate may transform into ammonium nitrite, which is not stable and may cause the risk of explosion (HIP-Azotara, 2015).

Table 4 - Classification of ammonium nitrate 34.8% N (HIP-Azotara, 2015)

Hazard class and category	Hazard statements
Oxidizing solid 3	Physical hazards: H272 (May intensify fire; oxidizer)
Eye irritation, category 2	Health hazards: H319 (Causes serious eye irritation)

5. AMMONIUM NITRATE STORAGE

In many Countries there are specific legal requirements which must be followed regarding ammonium nitrate storage. These requirements generally cover the storage areas with respect to their structural and operational requirements and must be consulted for the relevant Country (European Fertilizer Manufacturers′ Association, 2000).

Ammonium nitrate is stable if kept in original containers in storage areas with natural ventilation and if protected against fire, ignition sources, wet floors and exposure to the atmosphere (HIP-Azotara, 2015). Ammonium nitrate is an oxidizing material that, at elevated temperatures, will support the combustion of materials such as wood, paper, fuel oil and sulphur; but self-sustaining burning reactions are not usually obtained unless more than one percent of combustible material is present (Canadian Legal Information Institute, 2015).

The storage area must be dry and well ventilated. The stored product must not be directly exposed to sunlight in order to avoid physical damage due to thermal decomposition. Smoking in the storage area is strictly forbidden.

Incompatible materials for storage of ammonium nitrate are ignitable materials, reducing agents, acids, alkalies, sulphur, chlorates, chlorides, chromates, nitrites, permanganates, metallic powders, substances containing metallic powders such as copper, nickel, cobalt, zinc and their alloys (HIP-Azotara, 2015).

Electrical installation in storage area must be resistant to ammonia vapors.

Explosives, solid or liquid substances susceptible to decomposition by explosion, for example. organic peroxides or flammable liquids such as gasoline, benzene, toluene, ether, etc should not be stored in any warehouse or a part of a warehouse next to the one containing the AN (Kričak et al. 2010).

Organic substances, acids and other corrosive liquids and reactive substances such as chlorates, hypochlorites, chromates, nitrites, permanganates, zinc and its salts must not contaminate the AN in any case.

It should take care particularly to avoid contact AN with products that produce heat in a presence of moisture; quicklime, calcium cyanamide, slag as well as the products with poorly defined or undefined composition whose behavior in relation to the AN may be unsafe for example. pesticides, disinfectants, agents for the destruction of living organisms in the wood, etc. (Kričak et al. 2010).

Preferably, AN should be stored in closed warehouse.

The bags should be carefully put together in a pile, so that all sides can easily approach them. Piles should not be too close to walls or partition walls - at a distance of not less than 75 cm. Packaging requirements of AN are much stricter than those for fertilizers because of the hygroscopic properties of AN and the need for avoiding any danger that may occur due to spills of materials. Bags used for packaging of AN must be waterproof and sealed well to prevent entry of moisture. It must be strong enough to be able to withstand the damage during normal handling operations. At temperatures up to 55°C the bags must not show any signs of damage.

Water should be available near the warehouse in large quantities for immediate use.

6. AMMONIUM NITRATE ACCIDENTS

Although ammonium nitrate is not classified as explosive, there are many explosions incurred as a result of the fire of ammonium nitrate. The conditions necessary for an explosion were being examined in detail and it was quite certain that

Table 5 - Significant Accidents Involving Ammonium Nitrate - Post 1950 (Heather, 2002)

Date/ Place	Activity/Description	Product	Accident Type/ Casualties
1954 Red Sea	Sea Transport. Fire in ships hold, AN fertiliser + paper + organic/copper product. Explosions, ship abandoned and destroyed.	AN Fertiliser	Fire, Explosion. No injury.
1960 Traskwood, USA	Rail Transport. Wagons derailed, fire. Hydrocarbons cone, nitric acid and AN involved. Explosion.	AN Fertiliser	Fire, Explosion. No injury.
1966 USA	Storage. AN fertiliser, also pesticides and combustible materials. Fire. Smoke affected fire fighters. Explosion.	AN Fertiliser	Fire, Explosion. No injury.
1972 Australia	Road Transport. Semi-trailer with low density AN on fire, also oil load, too remote for fire fighting. Explosion.	AN Industrial	Fire, Explosion. 3 killed.
1972 France	Road Transport. AN solution tanker. Decomposition in lagging. Contaminated with organics & AN, explosion, hot AN solution released.	AN Solution	Fire, Explosion. Several passengers fatally injured.
1973 USA	Storage. Severe fire in AN store of wooden structure, fuel tank in payloader. Difficulty with fire fighting. A few tones of AN exploded. Main heap - 14000 t, unaffected.	AN Fertiliser	Fire, Explosion. No injury.
1975 Germany	Storage. SSD in bulk NPK initiated by welding, 1000 residents evacuated.	NPK Fertiliser	Fire, Explosion. No injury.
1997 Brazil	Road Transport. Truck loaded with AN caught fire and stopped on side of a narrow road. A petrol tanker tried to pass, caught fire and exploded. Subsequent AN detonation probably triggered by an exploding propane bottle on the trailer. A coach full of passengers was parked close to the scene of incident. Several passengers fatally injured.	AN Industrial	Fire, Explosion. Several passengers fatally injured.

confined space and high temperature are key elements for the explosion of AN in fire conditions (Kričak et al. 2010).

The content of organic substances increases the sensitivity of AN, allowing the explosion even at a lower pressure and a lesser degree of coating. Warm AN is especially sensitive to contamination by organic or other combustible materials, especially when in the closed-limited space. Table 5 presents some of the Significant Accidents Involving Ammonium Nitrate - Post 1950 (Heather, 2002).

Fire and subsequent explosions incidents from 2003 to 2004 are listed in Table 6.

Table 6 - Fire and subsequent explosions incidents 2003 – 2004 (Nygaard, 2006)

Date/place	Description
October 2, 2003 St. Romain en Jarez, France (TF 1, 2003)	Explosion in farmer's barn. The hay in a farmer's barn caught fire. The barn also contained some 3 000 kg to 5 000 kg fertilizer grade AN and about 3 000 plastic (polyethylene) boxes in piles. Approximately one hour and fifteen minutes after the fire was notified, an explosion took place causing 26 injuries (including 18 fire-men) and structural damage to 82 houses of varying severity. Damage was observed as far as 650 meter from the warehouse.
February 18, 2004 Neyshabur, Khorasan province Iran (BBC, 2004)	Railcar explosion. 51 run-away train wagons derailed, of which 7 wagons were loaded with 420 t fertilizer AN in bags, 7 with 390 t urea in bags, 17 with crushed-in-bulk sulphur, 10 with gasoline and fuel oil, and 10 with cotton lint. The AN exploded after catching fire from sulphur and petroleum products, causing 300 fatalities. 9 railway employees were charged for negligence.
March 9, 2004 Castellon, Spain (ThinkSpain, 2004)	Truck explosion. A truck with 25 t of fertilizer AN in bulk (open truck, metal "bath-tube") collided with a car and rolled over on its back, with spill of fuel and a fire started. About 20-30 minutes later an explosion occurred. Two people were killed (the car driver and a truck driver which was hit by a stone in the explosion) and 5 injuries. Pieces were thrown 200 meters away.
May 24, 2004 Mihailesti, Romania (Highbeam Research, 2004)	Truck explosion. A truck with 23 t of fertilizer AN in bags skid off the road and turned over. The truck cabin started burning. An hour later the cargo exploded, just when a fire crew was about to start the water hoses. 20 people were killed and several houses in nearby village were damaged. Neither the truck nor the driver was qualified for dangerous goods transport.
April 22, 2004 North Korea Ryongchon (GlobalSecurity, 2004)	Railcar explosion. An oil road tanker was reported to have collided with two railcars loaded with AN and knocking down an electric pole. It is thought that electric sparks caused a fire and explosion of the AN, with 161 fatalities and 1300 injuries. Due to the size of the crater officials have questioned whether military explosives were involved instead of AN.

6.1. Three Significant Ammonium Nitrate Accidents

6.1.1. Basf Plant Oppau, Germany, September 21, 1921

Ex explosives factory now making fertiliser – a 50/50 mixture of ammonium sulphate and ammonium nitrate called "mischsaltz" (Safety In Engineering, 2013). This highly hygroscopic mixture had the disadvantage of clogging together under the pressure of its own weight during storage. It was common practice to loosen the "aggregated" product by firing explosives in holes drilled using a jumper bar in the hardened mass (French Ministry of Sustainable Development, 2008).

On the morning of September 21^{st}, 1921, 4 500 tonnes of ammonium sulphonitrate were stored in the shop. The shop called "silo 110" is a 60 m x 30 m x 20 m half-buried building that is 4m below the ground. On the previous day, several firings were carried out in the building to use up a portion of the fertilizer. When the technician was preparing the holes for the firings in the "silo 110" a very powerful explosion took place creating a 90 m x 125 m crater and 20 m deep.

According to witnesses, there were two successive explosions, the first one being weak and the second one devastating. Seismographic readings from Stuttgart, at 150 km from Oppau also showed two distinctive explosions that occurred at an interval of half a second where the badly damaged buildings within 6 km (French Ministry Of Sustainable Development, 2008). How much was charged when the explosion occurred never learned because there were no witnesses, they have all died.

The explosion was heard in Munich, 275 km from the plant and caused panic among the masses. Material damage was reported at several dozens of kilometers away from the accident site. The entire region was then covered in thick smoke that along with the interruption of telegraph and telecom services made rescue operations even harder (Safety In Engineering, 2013).

The official human casualty reported included 561 deaths, 1 952 injured and 7 500 people left homeless. Among the victims include passengers from three worker trains arriving on site for change of shift. Around 80% of the buildings in Oppau were destroyed (French Ministry of Sustainable Development, 2008).

Figures 1, 2 present the consequences of explosion caused by blasting of hardened fertilizer in Opau, Germany, 1921.

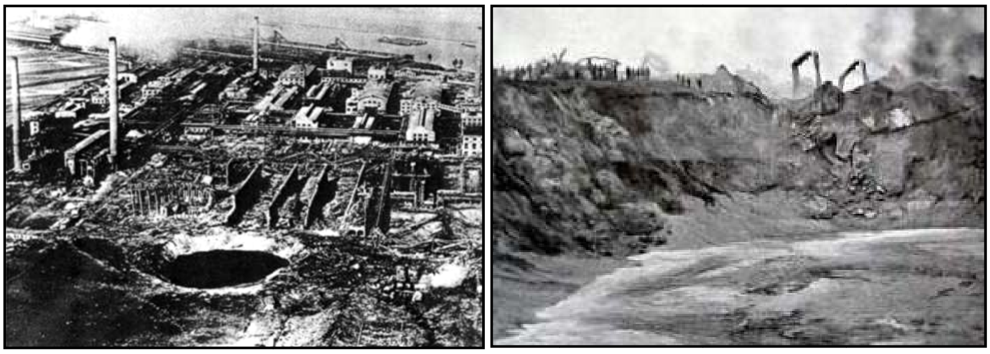

Figure 1 - The consequences of explosion caused by blasting of hardened fertiliser, Opau, Germany, 1921 (French Ministry of Sustainable Development, 2008)

According to an article in the New York Times dated January 29, 1922, the material damage was assessed at 321 000 000 DM, i.e. 1 700 000 US$ (French Ministry of Sustainable Development, 2008).

Until this accident it was believed that ammonium nitrate are not accepted and is not supported by the detonation. In this case, ammonium nitrate acted as inert matter. However, ammonium nitrate under certain circumstances accepts detonation form of decomposition especially when the initial external impulse i.e. activation energy from other explosive exists. Regardless of whether AN is clean or in a mixture with inert or is a part of the complex fertilizer, the explosive should never be used for loosening the hardened mass.

Figure 2 - The consequences of explosion in Opau, Germany, 1921
(French Ministry Of Sustainable Development, 2008)

6.1.2 Texas City, April 16, 1947

Ammonium nitrate loaded on ships for further transport caught fire. Some water and an extinguisher were used to fight the fire, but hoses were not employed for fear of ruining the cargo (History, 2015). The crew attempted to restrict oxygen but they did not realize that because of ammonium nitrate's chemical composition, it does not require oxygen in order to burn. Fire on board led to explosion of some 2 000 tones of ammonium nitrate. Chain reaction explosions occurred on other ships and at oil storage facilities (Safety In Engineering, 2013). The force of the explosion lifted another ship right out of the water (History, 2015). People working at the docks were killed instantly. Pieces of flaming debris damaged the oil refineries in the area. A nearby chemical storage facility also exploded, killing 234 of the 574 workers there. A residential area of 500 homes was also leveled by the blast. In all, 581 people died and 3 500 were injured. The explosion caused 100 million US$ in damages (History, 2015). Figure 3 presents an aerial view of the place where the explosions occurred.

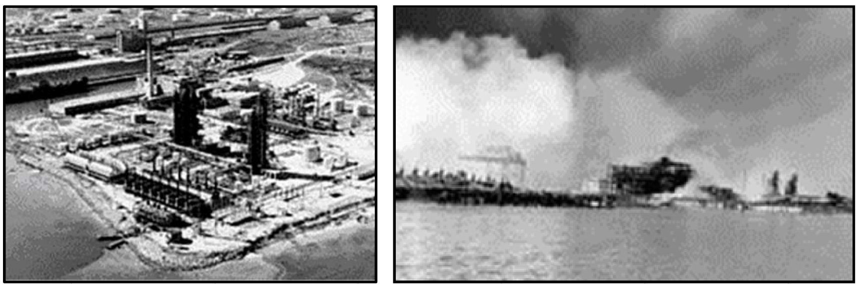

Figure 3 - An aerial view of the place where the explosions occurred in Texas City, 1947
(Kričak et al. 2010)

In this case, AN was affected by a fire in an enclosed space without the possibility of leakage of dissolved AN, which accelerated the growth of temperature and pressure conditions and turned the fire into the explosion (Kričak et al. 2010). AN was packed in paper bags and coated with a 1% wax used as an anticaking agent, which increased the explosive sensitivity of AN taken by fire and also the energy potential of explosion (Kričak et al. 2010).

6.1.3 AZF Toulouse Disaster, September 21, 2001

A fertiliser factory containing ammonium nitrate storage facilities exploded. The factory employed 470 persons, was located 3 km from the centre of Toulouse on an island of the Garonne River surrounded by an (urban) environment. The explosion produced a crater measuring about forty meters in diameter and 7 m in depth related to the natural ground (Safety In Engineering, 2013). About 200 t to 300 t is said to be involved in the explosion (Kričak et al. 2010). The exact cause remains unknown.

Figure 4 presents crater resulting from the detonation and the warehouse destroyed by the blast.

a) b)

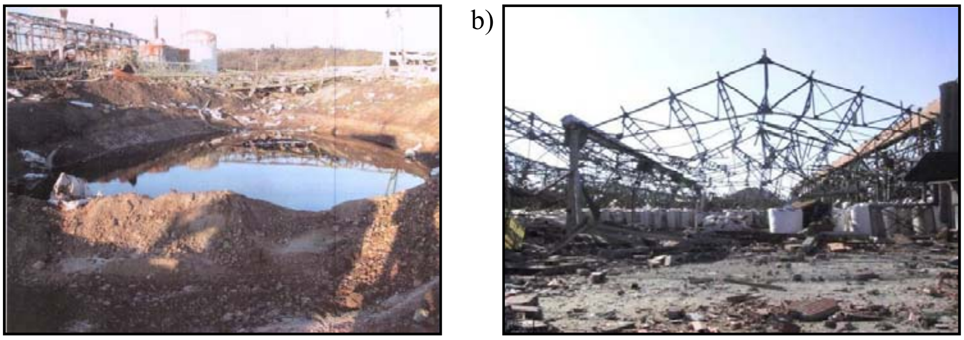

Figure 4 - a) Crater resulting from the detonation, b) Warehouse destroyed by the blast (French Ministry of Sustainable Development, 2013)

Explosion equivalent to 3.4 on Richter scale. 22 people were killed on the factory site and 8 persons outside. In total 2 500 persons were injured. Various structures were distorted within a radius of 400 m to 700 m. Buildings were damaged within a radius of 700 m to 1 500 m and many windows broken even at a larger distance (Safety In Engineering, 2013).

In total about 30 000 buildings were touched of which 10 000 heavily damaged including schools, Universities and a hospital. Transportation facilities and electrical power lines and telephone communication were also disrupted. The financial consequences were estimated to be 2.5 billion euros.

The last three accidents represent a real disasters because of explosions of large amounts of ammonium nitrate. However, examples of accidents listed in Tables 5 and 6 show that the negligence in handling of ammonium nitrate during the transportation and storage may also cause fire or explosions.

7. TRANSPORT OF AMMONIUM NITRATE

For the purpose of transportation, ammonium nitrate with not more than 0.2% combustible substances, including any organic substance calculated as carbon, to the exclusion of any other added substance is classified as Class 5.1 (Oxidizers), (United Nations, 2009). Ammonium nitrate with more than 0.2% combustible substances, including any organic substance calculated as carbon, to the exclusion of any other substance is classified as an explosive (United Nations, 2009).

According to UN International Transportation Regulations for Dangerous Goods (United Nations, 2009):

- Classification of AN solid, non fertilizer: UN 1942;
- Classification of AN fertilizer: UN 2067.

Ammonium nitrate with 34.8% of N (HIP-Azotara, 2015) is classified as:

- Transport hazard class(es): ADR / RID / ADN: 5.1;
- Packing group: ADR / RID: III

8. LEGISLATION

Ammonium nitrate (AN) has drawn increased attention from authorities over the last years because of various accidents. Security issues are related to the safety of manufacture, handling, storage and transportation of ammonium nitrate. Some of relevant safety, health and environmental regulations of the Republic of Serbia regarding ammonium nitrate or AN fertilizer are:

- Regulations of technical normatives on handling and storage of solid fertilizers containing ammonium nitrate ("The Official Journal of the SFRY" no.55/91) – the provisions of art. 3 par. 5 and 6 of these Regulations cease to be effective upon the entry into force of the Regulations issued in "The Official Gazette of the RS" no.70/2010);
- Law on chemicals ("The Official Gazette of the RS", no. 36/09);
- Law on waste management ("The Official Gazette of the RS", no.36/09 and 88/10);
- Regulation on classification, packaging, labeling and advertising of chemical and certain article in accordance with Globally harmonized system of classification and labelling of the UN ("The Official Gazette of the RS", no.64/10, 26/11, 5/12 and 105/13);
- Regulations on storage, packaging and labeling of hazardous waste ("The Official Gazette of the RS", no.92/10);
- Regulations on conditions and manner of collection, transport, storage and treatment of waste which is to be used as secondary raw material or for obtaining energy ("The Official Gazette of the RS", no.98/10);
- Regulations on the contents of safety data sheet ("The Official Gazette of the RS", no.100/11);
- List of classified substances ("The Official Gazette of the RS", no.48/14).

9. CONCLUSIONS

Ammonium nitrate is a stable compound and generally is difficult to explode when it is in solid or molten form or in solution. However, ammonium nitrate may explode when it is exposed to strong shock or to high temperature under confinement. The presence of certain contaminants may increase the explosion hazard of ammonium nitrate. While certain inorganic contaminants, including chlorides and some metals, such as chromium, copper, cobalt, and nickel may sensitize ammonium nitrate, organic impurities increase the energy of ammonium nitrate explosions. As ammonium nitrate solution becomes more acidic, its stability decreases, and it may be more likely to explode.

In a large quantity of ammonium nitrate, localized areas of high temperature may be sufficiently confined by the total quantity to initiate an explosion. The explosion of a small quantity of ammonium nitrate in a confined space (e.g., a pipe) may initiate the explosion of larger quantities (e.g., in an associated vessel).

Low density areas, such as bubbles, in molten ammonium nitrate or solutions, also may increase the possibility of an explosion and enhance the propagation of an explosion.

Ammonium nitrate by itself does not burn, but in contact with other combustible materials, it increases the fire hazard. It can support and intensify a fire even in the absence of air. Fires involving ammonium nitrate can release toxic nitrogen oxides and ammonia. A fire involving ammonium nitrate in an enclosed space could lead to an explosion.

ACKNOWLEDGEMENT

The authors thank the Serbian Ministry of Education, Science and Technological Development for their support on the Project of Technological Development TR33003.

REFERENCES

[1] BRITISH BROADCASTING CORPORATION (2004) *Iran train blast kills hundreds* [Online]. Available from: http://news.bbc.co.uk/2/hi/middle_east/3498851.stm [02/04/15].

[2] CANADIAN LEGAL INFORMATION INSTITUTE (2015) *Ammonium Nitrate Storage Facilities Regulations, Statutes and Regulations* [Online]. Available from: http://www.canlii.org/ca/regu/crcl145/part57046.html [05/18/15].

[3] COMPRESSED GAS ASSOCIATION (1963) *Standards for solid ammonium nitrate. (Nitrous Oxide Grade, Specifications, Properties and Recommendations For Packaging, Transportation, Storage and Use)*. 2nd ed. New York: Compressed Gas Association Inc.

[4] EUROPEAN FERTILIZER MANUFACTURERS′ ASSOCIATION (2000) *Production of Ammonium Nitrate and Calcium Ammonium Nitrate*, *Booklet No. 6* [Online]. Available from: http://www.fertilizerseurope.com/fileadmin/user_upload/user_upload_prodstew/documents/Booklet_nr_6_Production_of_Ammonium_Nitrate_and_Calcium_Ammonium_Nitrate.pdf [15/04/15].

[5] ELVERS, B. (1989) *Ullmann's Encyclopedia of Industrial Chemistry, Vol. A2*. 5th ed. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, pp.243-252.

[6] FRENCH MINISTRY OF SUSTAINABLE DEVELOPMENT (2008) *Explosion in a nitrogenous fertiliser plant 21 September 1921 Oppau Germany* [Online] Available from: http://www.aria.developpement-durable.gouv.fr/wp-content/files_mf/FD_14373_oppau_1921_ang.pdf [04/10/15].

[7] FRENCH MINISTRY OF SUSTAINABLE DEVELOPMENT (2013) *Explosion in the AZF fertilizer plant September 21st, 2001 Toulouse France* [Online] Available from: http://www.aria.developpement-durable.gouv.fr/wp-content/files_mf/FD_21329_TOULOUSE_DP_JLC_GB_29072013.pdf [05/03/15].

[8] GLOBAL SECURITY (2004) *Train-wreck and Explosion* [Online] Available from: http://www.globalsecurity.org/military/world/dprk/ryongchon-imagery.htm [05/02/15].

[9] HEATHER, D. (2002) A review of past ammonium nitrate accidents and lessons learned. In: *Presentation at the "Workshop on Ammonium Nitrate", Ispra, January 2002.* Ispra: European Fertilizer Manufacturers Association.

[10] HIGHBEAM RESEARCH (2004) [Online] Available from: http://static.highbeam.com/u/unitedpressinternational/may242004/ [05/25/04].

[11] HIP-AZOTARA (2015) *Safety Data Sheet - Ammonium Nitrate 34.8%N.* Pančevo: HIP- Azotara.

[12] HISTORY (2015) *1947 Fertilizer explosion kills 581 in Texas* [Online] Available from: http://www.history.com/this-day-in-history/fertilizer-explosion-kills-581-in-texas [04/12/15].

[13] KRIČAK, L. et al. (2010) Basic principles of handling ammonium nitrate (In Serbian). In: *Proceedings of the 9th International Scientific Conference OMC 2010, Vrnjačka Banja, October 2010.* Belgrade: Yugoslav Opencast Mining Committee, pp.100-109.

[14] MELLOR, J. (1922) *A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol.* 2. London: Longmans Green.

[15] NYGAARD, E.C. (2006) *Safety of Ammonium Nitrate*. Porsgrunn: International Society of Explosives Engineers.

[16] SAFETY IN ENGINEERING (2013) *Three Significant Ammonium Nitrate Accidents* [Online] Available from: www.safetyinengineering.com [05/07/15].

[17] SUSLICK, K. (1992) *Kirk-Othmer Encyclopedia of Chemical Technology, Vol.2*. 4th ed. New York: John Wiley & Sons, pp.698–705.

[18] TÉLÉVISION FRANÇAISE 1 (2003) [Online] Available from: http://www.lci.fr/news/france/2003/0,,1394620-VU5WX0lEIDUy,00.html [10/03/03].

[19] THINKSPAIN (2004) Lorry explodes after collision in Castellón [Online] Available from: http://www.thinkspain.com/news-spain/3324 [02/11/15].

[20] UNITED NATIONS (2009) *Recommendations on the Transport of Dangerous Goods, Model Regulations*. 16th ed. [Online] Available from: http://www.unece.org/fileadmin/DAM/trans/danger/publi/unrec/rev16/English/Volume1.pdf [04/12/15].

[21] US DEPARTMENT OF COMMERCE (1972) *Hazards of Chemical Rockets and Propellants Handbook Vol. 2, Solid Rocket Propellant Processing, Handling, Storage and Transportation*. Springfield: National Technical Information Services.