Ammonium nitrate explosions. Case study: the Mihăilesti accident (2004), Romania

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Abstract. Ammonium nitrate is used both as a fertilizer in agriculture and as an ingredient for industrial explosives (for open pits, mine tunnels etc.). The substance is stable in normal conditions of use, storage and transportation, but in the spite of this stability several accidents occurred in the last century involving large quantities of ammonium nitrate, causing many fatalities and human injuries. This paper analyses in more detail the transportation accident with ammonium nitrate explosion in 2004 at Mihăilesti village, Buzău County, Romania. Based on the official report about the accident conditions and consequences, different scenarios were considered using different TNT equivalency factors and the physical effects of the explosion were determined.
Key Words: ammonium nitrate, explosion, Mihăilesti, TNT equivalency.

Introduction. Ammonium nitrate (AN) - NH_4NO_3 – is used both as a fertilizer in agriculture and as an ingredient for industrial explosives (for open pits, mine tunnels etc.). It is an oxidizing agent which has a good resistance to detonation, but if heated to high temperatures in closed spaces can lead to violent reactions and explosions, in particular if it is contaminated or mixed with different materials, such as combustibles, acids, bases, chlorides etc. (Martel 2004; UNIDO 1998).

AN is a colourless salt, forming hygroscopic rhombic crystals. It has a good solubility in water: at 0°C 118 g of AN, at 20°C 150 g of AN, at 25°C 214 g of AN and at 100°C 870 g of AN can be solved in 100 g of water (Patnaik 2003).

The AN based fertilizer has a high density and a reduced porosity. This structure allows maintaining intrinsic physical properties from production to use in agriculture, passing through various intermediate stages including transportation and storage. The substance is stable in normal conditions of use, storage and transportation. Low density AN used for the production of explosives is especially produced with high porosity for better absorption of the oils, which leads to greater sensitivity to detonation.

Potential hazards associated to ammonium nitrate. AN has a very complex behaviour and presents the main three types of hazards:

- instability during decomposition and toxic gas formation;
- fire due to the strong oxidizing property and toxic gas formation;
- explosion.

The most important parameters influencing the above mentioned hazards are: contamination, porosity and density of particles.

Pure AN starts to decompose if heated over a specific temperature, releasing toxic gases such as nitrogen oxides and ammonia. If the heat source is removed and the space is ventilated the decomposition process stops. Several chemical reactions can occur during decomposition. The main reactions are the following:

- between temperature range 170–250°C: $NH_4NO_3 \rightarrow NO_2 + 2H_2O + 37$ kJ/mol;
- between temperature range 250–292°C: $NH_4NO_3 \rightarrow NH_3 + HNO_3 - 174$ kJ/mol;
- at higher temperatures: $NH_4NO_3 + 2NO_2 \rightarrow N_2 + 2\,HNO_3 + H_2O + 232$ kJ/mol
  $2NH_4NO_3 \rightarrow 2\,N_2 + 4H_2O + O_2 + 118$ kJ/mol.

AN is not a flammable substance, but due to its oxidizing property can maintain and intensify combustion without the presence of air, therefore the fire involving AN cannot be extinguished by suffocation. Water is the best substance which can be used in this case by flooding the whole fire compartment. During a fire AN decomposes forming the above mentioned toxic gases (HSE 2012).

The melting point of pure AN is at 169.6 °C and during the melting a part of the heat is absorbed. Moreover, the melted AN can flow away from the source of fire and the heat is transferred to the ground and atmosphere. The melted AN is more sensible to detonation and any heavy object falling into the pool can initiate an explosion.

The composition of gases released during decomposition depends on the composition of the fertilizer. The main substances released during the decomposition of AN based ferilizers are (EFMA 2007):

a) After Perbal's classification:
   - water vapour (H_2O): 45-65%;
   - nitrogen (N_2): 19-26 %;
   - nitrous oxide (N_2O): 7-20%;
   - hydrogen chloride (HCl): 0.5-10%
   - nitrogen oxides (NO_x): 0-9%;
   - ammonium chloride (NH_4Cl): 0-7%;
   - chlorine (Cl_2): 0-2%.

b) After Kiiski's classification:
   - water vapour (H_2O): 56%;
   - nitrogen (N_2): 20%;
   - nitrous oxide (N_2O): 11%;
   - chlorine (Cl_2) and hydrogen chloride (HCl): 6%;
   - nitrogen oxides (NO_x), ammonia (NH_3) and hydrogen fluoride (HF): 7%.

Accident involving ammonium nitrate. Several acccidents occured in the last century involving large quantities of AN or AN based materials (fertilizers, ANFO etc.). In a literature review made by Pittman et al (2014) 12 major accidents are presented and a list of 10 lessons are discussed. Eight from the presented accidents involved fatalities and human injuries, and 5 of the 12 accidents occured in case of transportation (2 by railcars and 3 by road trucks).

One of the accidents presented in the above mentioned work is the Mihăilesti (2004) accident, which will be discussed and analysed in more detail in this paper. The description of the accident is based on the official report of the Buzău County Civil Protection Inspectorate (2004), completed with journal articles and a Youtube documentary film.

The aim of the paper is to present the physical effects analysis of ammonium nitrate explosion using different TNT equivalents found in literature.

Case study: the Mihailesti explosion (2004), Buzau County, Romania. In the early morning of 24th May 2004 at the entrance of Mihăilesti village a road truck transporting 20 t of ammonium nitrate skidded off the road, overturned in the ditch and slipped several meters. The cabin of the truck caught fire in a few minutes after the impact. The ammonium nitrate was transported in sacks, from which in the moment of the impact some flew off the trailer and many of them got broken releasing the substance on the ground.

The driver of the truck reported the accident to the police and tried to extinguish the fire in the cabin. Civilians travelling on the road and local people from the village stopped to help him extinguish the fire, but without success. The fire was spreading due to the strong oxidizers presence. Also two reporters from the Antena 1 station were present filming the event. Later two special fire-fighter trucks arrived and started to prepare the equipment for the intervention, but the explosion took place before they could start to extinguish the fire.

The explosion took place approximately after 1 h from the moment of the impact. The Istria seismological station (aprox. 160 km from Mihăilesti) registered two earthquakes, the first at 05:47:44 and a second, much stronger at 05:48:45. The second earthquake was comparable to a 3 MSK earthquake originating from the Vrancea area. The results show the fact that probably two explosions took place consecutively, the second one being much stronger (Jurnalul de Buzau 2011; Revista 22 2004).

The consequences of the accidents were catastrophic:

- 18 deaths (fire-fighters, local people, reporters, policemen), 11 injured;

- 150 m of E85 road destroyed;
- 16 houses damaged: windows broken or roof damaged;
- 6 private cars damaged or destroyed;
- 2 fire-fighter trucks heavily damaged;
- electrical supply network of Mihailesti village damaged.

Heavy pieces from the truck were projected at hundreds of meters, the central axle of the truck weighting 1.5 t being found in the roof of a house at 250 m from the accident.

Based on the above presented data, simulations of the explosion were performed using TNT equivalency model, considering different TNT equivalency factors. The TNT equivalency model is widely used for the estimation of physical effects of explosions, considering a certain equivalency factor for the specific substance (HSE 2012).

In scientific literature different TNT equivalency factors can be found for fertilizer grade ammonium nitrate (FGAN): 3% (Kersten & Mak 2004), 15% (GHD 2012). These equivalency factors were selected for the analysis of physical effects of an explosion. The results of overpressure versus distance are presented in Figure 1.

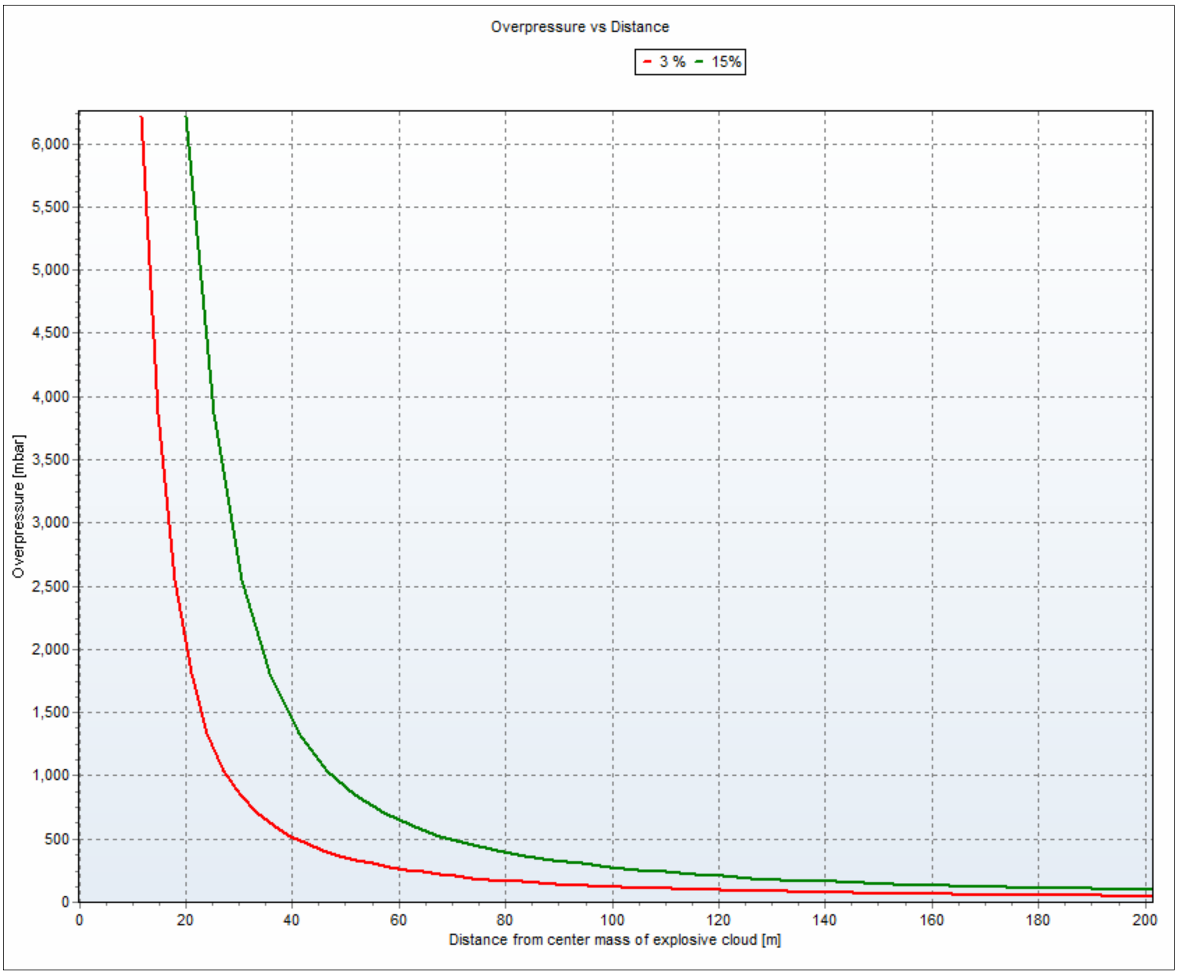

Figure 1. Overpressure versus distance in case of AN explosion using 3% (red) and 15% (green) TNT equivalency factors.

For the analysis of consequences (in terms of physical effect of overpressure causing harm to human - Table 1) of AN explosions the overpressure limits presented in the Guide for the evaluation of Safety Reports (GIES 2009) were selected, as follows:

- 140 mbar for beginning of lethality;
- 300 mbar for high lethality due to indirect effects of explosion (falling objects, rooftop collapse);
- 600 mbar for high lethality due to direct effects of overpressure.

Table 1

Physical effects of an explosion in function of TNT equivalency

Physical effects/ TNT Equivalency	*Beginning of lethality – 140 mbar*	*High lethality due to indirect effects – 300 mbar*	*High lethality due to direct effects – 600 mbar*
3 %	91 m	56 m	36 m
15 %	156 m	95 m	62 m

The results show a high difference in the distances obtained in the simulations using different TNT equivalency factors for the explosion. It can be seen that the difference in distances is bigger in case of lover overpressures.

Conclusions. A general conclusion of the authors is that both accidental and deliberate accidents will continue to occur unless best practices are implemented in industry and transportation and unless lessons learned from past accidents are applied.

Considering the earthquakes measured at Istria station it can be concluded that two explosions took place in the case of Mihăilesti accident. The first explosion was weaker and a lower TNT equivalency could be associated with it. The second explosion was probably a detonation and a high TNT equivalency should be associated.

A more detailed analysis of the Mihăilesti explosion is necessary for the determination of TNT equivalencies.

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