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Research paper / Praca doświadczalna

The effect of chemical and physical properties and particle morphology of granulated ammonium nitrate on the composition of post-explosion gases and detonation velocity of ammonium nitrate fuel oils
Wpływ właściwości fizykochemicznych oraz morfologii ziaren granulowanej saletry amonowej na skład gazów postrzałowych i prędkość detonacji saletroli

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Abstract: *The results of studies of three grades of ammonium nitrate(V): granulated fertiliser grade and granulated porous "Standard" and "Extra" grades, are presented. The chemical and physical properties and particle morphology of the analysed ammonium nitrate grades were studied. The content of hazardous oxides (CO, NO_x) in the gases formed in the explosion of ammonium nitrate(V) fuel oils (ANFO) containing ammonium nitrates and 5.7% of oil was determined as was their detonation velocities.*
Streszczenie: *W pracy przedstawiono wyniki badań trzech typów saletry amonowej: granulowanej rolniczej oraz granulowanych porowatych typu „Standard" i „Extra". Wykonano badania właściwości fizykochemicznych i morfologii ziaren testowanych gatunków saletr amonowych. Przeprowadzono pomiary zawartości szkodliwych tlenków (CO, NO_x) w gazach postrzałowych saletroli zawierających ww. saletry amonowe i 5,7% oleju. Wyznaczono prędkości detonacji testowanych saletroli.*

Keywords: *ammonium nitrate(V) fuel oils, ANFO, grain morphology, post-explosion gases, detonation velocity*
Słowa kluczowe: *azotan(V) amonu, saletrole, morfologia ziaren, gazy postrzałowe, prędkość detonacji*

1. Introduction

Ammonium nitrate(V) fuel oils (ANFOs) are one of the least complex explosives, mostly used in open-cast mines. Although, the first ANFO variants were developed many years ago, in the last decade many studies of the effect of different types of additives on their detonation properties [1-5], density [6], temperature [7] and detonator mass [8] on the detonation velocity, have been carried out. Physical and chemical properties of alternative liquid combustible components of ANFOs [9-12] and the morphology of their basic component – ammonium nitrate(V) [13, 14] were also studied.

In Poland, for many years, ANFO production was based on a standard ammonium nitrate(V), commonly used as a fertilizer. The low porosity of this material resulted in poor product quality due to the displacement of liquid organic fuel (oil), causing oil accumulation in the charge in the bottom section of the blast hole. Oil sedimentation generates carbon monoxide in the bottom section of the charge, and due to oil imbalance, toxic nitrogen oxides, in the form of a brownish cloud, are formed in the top layers [15]. Currently, ANFOs are produced as a mixture of porous granulated ammonium nitrate(V) and mineral oil whose viscosity enables it to be absorbed by the oxidising agent granules. The particle morphology of ammonium nitrate(V) affects ANFO detonation velocity [16, 17] and determines the composition of its explosion products.

The purpose of the study was to determine the chemical and physical properties of three grades of ammonium nitrate(V): granulated fertiliser grade and granulated porous "Standard" and "Extra" grades and to determine the content of hazardous components (CO, NO_x) in the explosion products and detonation velocity of ANFOs containing those ammonium nitrates(V) and 5.7% of oil.

2. Experimental part

2.1. Determining chemical and physical properties of ammonium nitrates

Particle size distribution (Table 1), moisture content, oil absorption capacity, bulk density, helium density and total porosity (Table 2) were determined for the ammonium nitrate(V) grades being studied.

Table 1. Particle size distribution of ammonium nitrate(V) samples

Fraction [mm]	Granulated ammonium nitrate(V) (grade)		
	fertilizer	porous "Standard"	porous "Extra"
	[%]		
Above 2.0	73.6	17.7	1.9
1.0-2.0	20.8	81.9	97.2
0.8-1.0	2.9	0.3	0.8
0.5-0.8	2.1	0.1	0.1
Below 0.5	0.6	0	0
Total	100.0	100.0	100.0

The oil absorption capacity was determined by adding oil in 0.5 cm^3 increments to a 100 g sample of ammonium nitrate(V) until a non-bound and free oil was observed in the mixture. To determine the porosity of samples, the actual density, i.e. the density of a non-porous solid material was determined using the helium density method.

Table 2. Chemical and physical properties of ammonium nitrate(V) samples

Ammonium nitrate(V) grade	Moisture content [%]	Screen fraction [mm]	Oil absorption capacity [%]	Bulk density [g/cm^3]	Helium density [g/cm^3]	Porosity Total [%]
Fertilizer	0.01	0.5-2.0	1.5	0.96	1.72	44.1
Porous "Standard"			8.5	0.78	1.71	54.3
Porous "Extra"			14.5	0.69	1.74	60.2

The density decreases and the oil absorption capacity increases with increasing number of voids in the analysed samples (Table 2). The presence of pores was also verified by the determined total porosity which indicated that the porous "Extra" grade has the highest pore volume whereas the fertiliser grade has the lowest.

2.2. Analysis of the morphology of ammonium nitrate(V) samples and interpretation of SEM images

To show the morphology of the analysed samples, the internal and external structure of three ammonium nitrate(V) grades was analysed. The structural tests were carried out on samples of undamaged individual granules (external structure) and granules in their cross-section i.e. fractured (internal structure). The sectioned granules were placed on a support and coated with gold-palladium alloy using a low-energy Scancoat 6 sputter coater. Images were taken using a high-resolution Leo Zeiss 435 VP scanning electron microscope at a safe non-destructive voltage (15 kV), thereby avoiding significant heating of the samples. The following magnifications were used to obtain comparable images for the analysed samples: 50x, 150x, 500x and 1000x. If the samples did not fit in the SEM image, different magnifications were used. Figures 1-5 show the morphology of the sample grades.

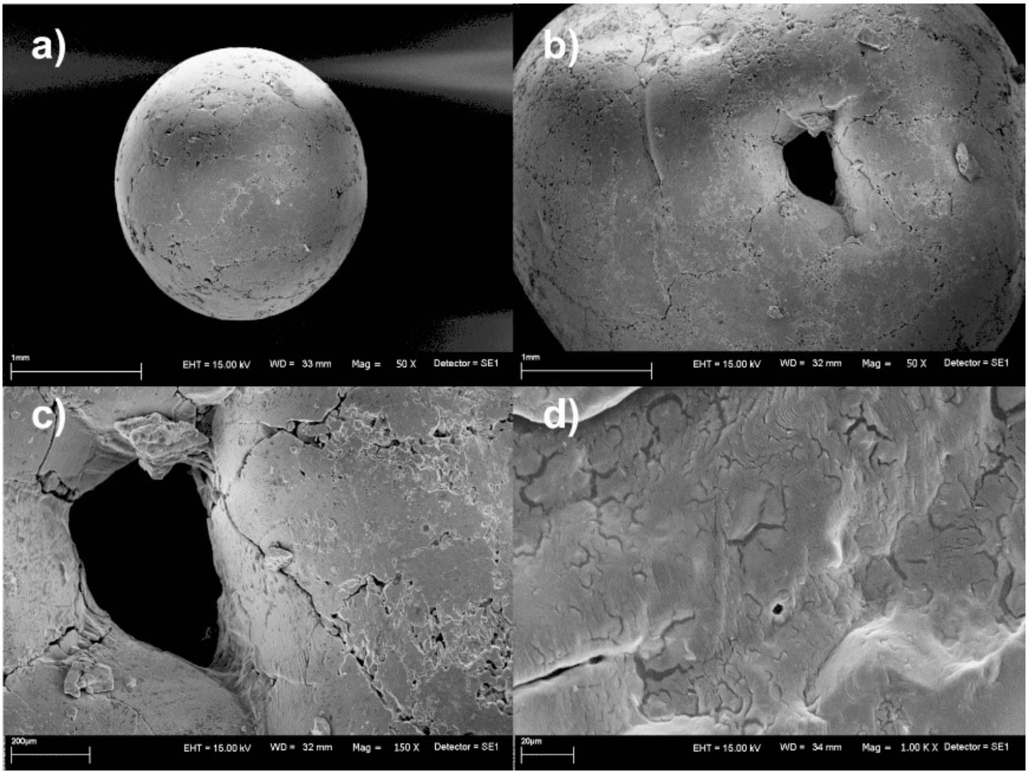

Figure 1. SEM images of external surface of non-porous ammonium nitrate(V) granules at: a) 50x, b) 50x – larger granule, c) 150x, d) 1000x

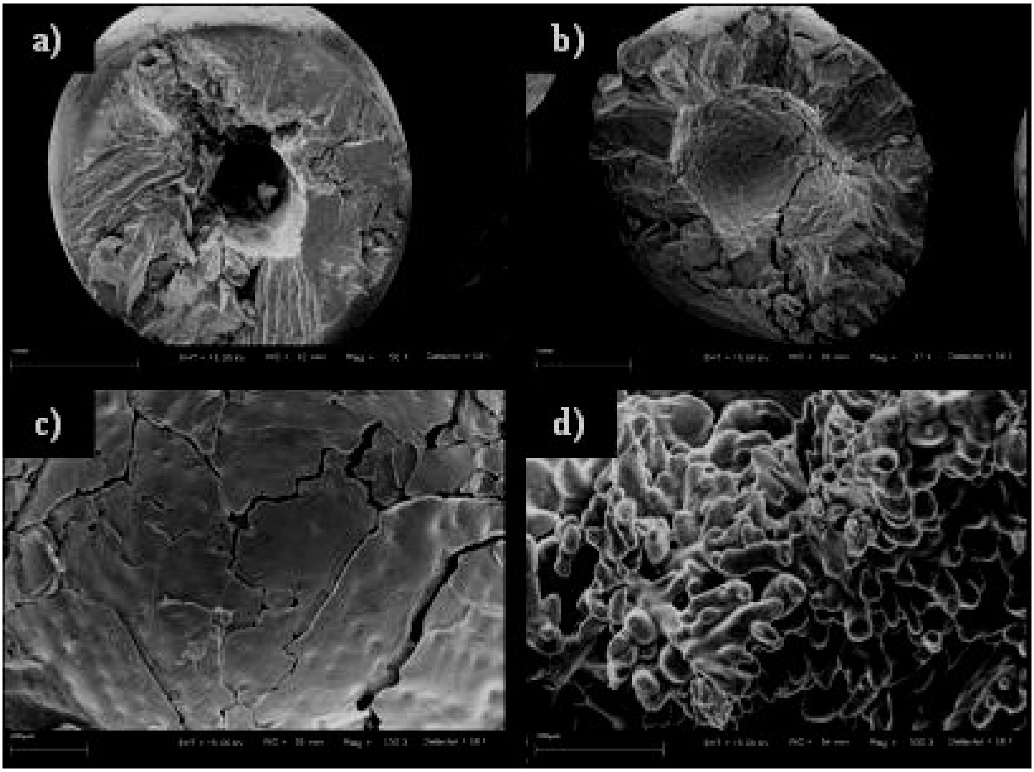

Figure 2. SEM images of fractured surface of non-porous ammonium nitrate(V) granules at: a) 50x, b) 37x, c) 150x, d) 500x

The non-porous ammonium nitrate(V) granules are seen to be spherical with a visible hole towards the centre of the granule – Figures 2a and 2b. The granules differ in size, and under the same magnification take up different areas (Figures 1a and 1b). The surface structure is compact with isolated cracks probably caused by stresses due to the solidification of a drop of liquid ammonium nitrate(V) during granulation (Figures 1b and 1c). At 1000x, no porous structure is observed at the granule's surface; it shows a uniform and smooth structure (Figure 1d). The images of cross-sections of non-porous granulated ammonium nitrate(V) particles, in most cases, show a central core (Figures 2a and 2b).

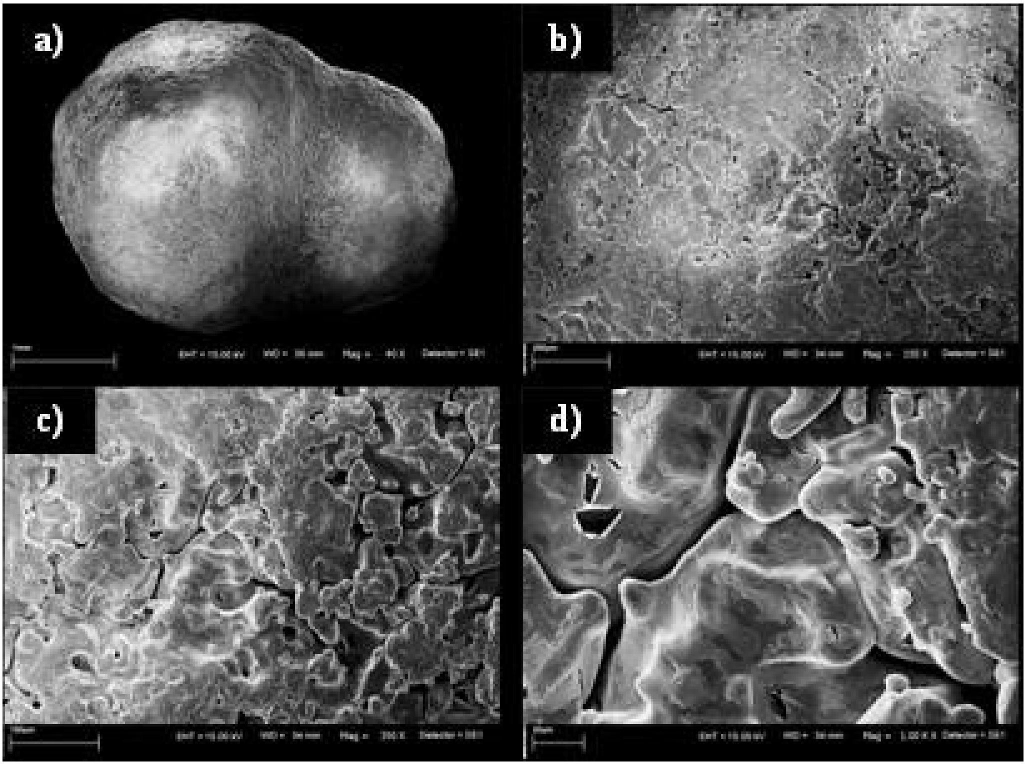

Figure 3. SEM images of external surface of porous ammonium nitrate(V) granule, "Standard" grade, magnification: a) 40x, b) 150x, c) 350 x, d) 1000x

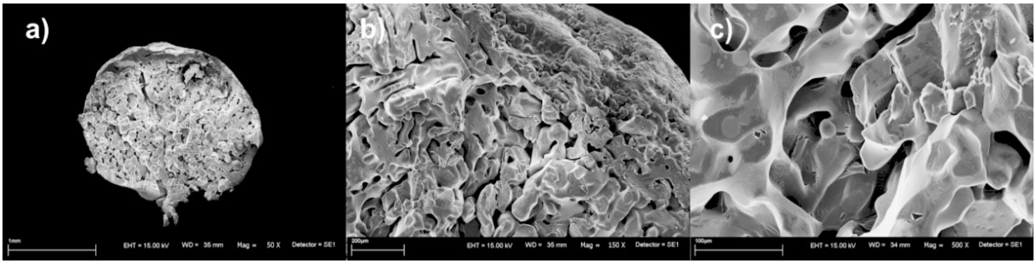

Figure 4. SEM images of cross-section of porous ammonium nitrate(V) granule, "Standard" grade, magnification: a) 50x, b) 150x, c) 500x

The "Standard" grade granules are usually spherical, however, irregular shapes were also observed (Figure 3a). The morphology of the surface of the granules shows high porosity, clearly visible at 50x magnification. The shape and size (~5 μm) of the pores are clearly visible in Figure 3d at 1000x. The cores are not visible and the material shows a similar structure in its entire cross-section (Figures 4a-c).

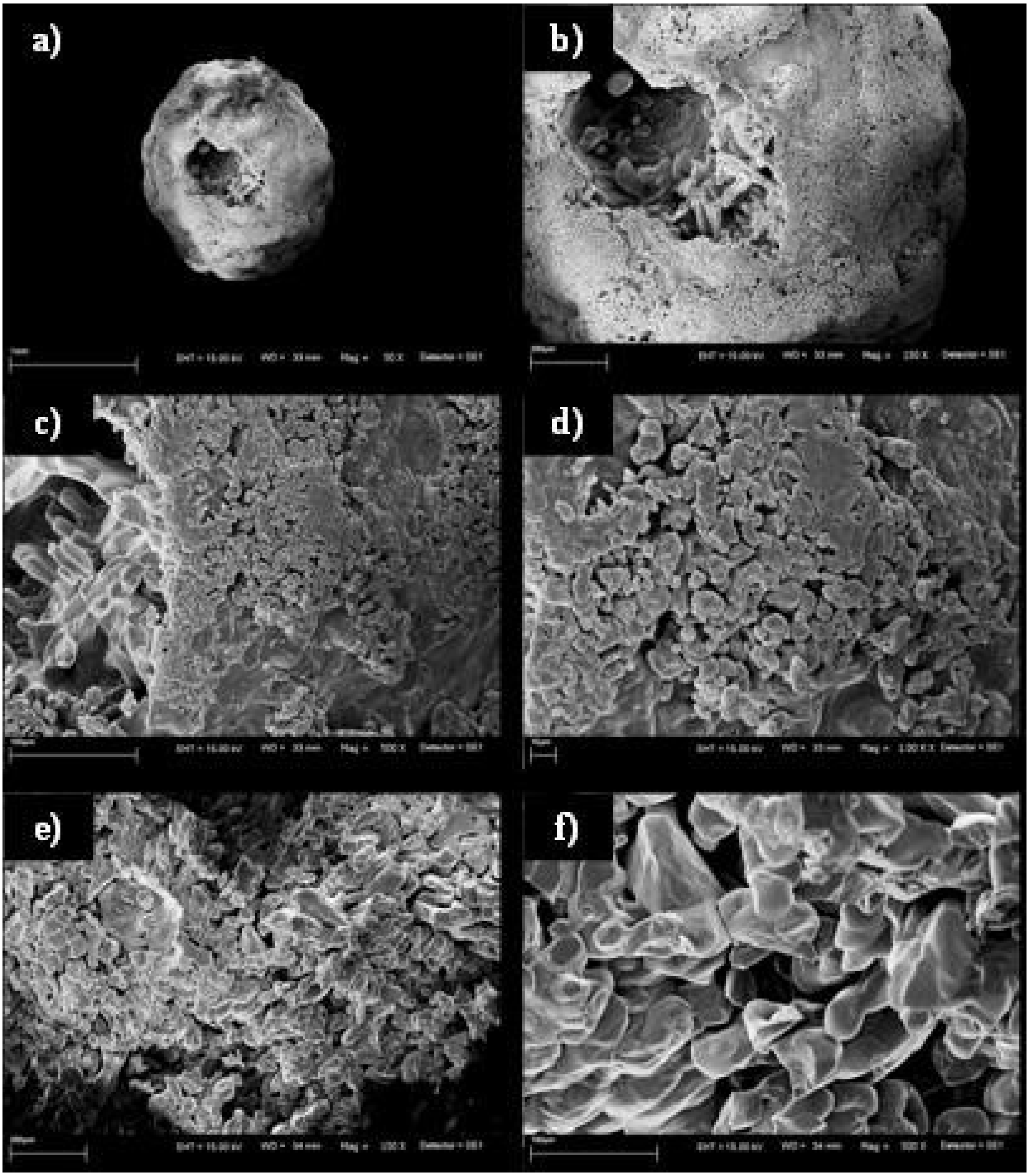

Figure 5. SEM images of porous surface of "Extra" grade ammonium nitrate(V) granule, magnification: a) 50x, b) 150x, c) 500x, d) 1000x, granule cross-section, magnification: e) 150x, f) 500x

The "Extra" grade granules are spherical. Figures 5a and 5b show a relatively large (0.5 mm diameter) hole towards the centre of the granule. High porosity can be observed on the surface of the analysed material with the pores evenly distributed over the entire surface (Figures 5c-d). The central part of the granule has similar morphology to the rest of the granule (Figures 5e and 5f).

2.3. Determining the content of hazardous explosion products

An analysis of the content of hazardous explosion products for ANFOs containing 5.7% oil, was carried out. The ANFO samples were obtained by mixing the components of the explosive composition. The experiments were carried out using the method described in [18, 19] in accordance with European standard EN-13631-16: 2004. The amount of each oxide was expressed in relation to 1 kg of the analysed ANFO. Based on Equation 1, the total amount of oxides was calculated and expressed as carbon monoxide equivalent (L_{CO}), using the coefficient 6.5 [20], allowing for the higher toxicity of nitrogen oxides. Table 3 shows the results of the analysis of post-explosion gases of the analysed ANFO grades.

$$L_{CO} = xCO + 6.5yNO_x \tag{1}$$

where x – volume of carbon monoxide in litres, y – volume of nitrogen oxide in litres.

Table 3. The amount of toxic oxides in post-explosion gases of ANFO samples prepared using different ammonium nitrate(V) grades.

Ammonium nitrate(V) grade in ANFO	Released oxides Q_g [l/kg]				
	CO	NO	NO_2	NO_x	L_{CO}
Non-porous fertilizer	18.7	8.2	7.7	15.9	122.05
“Standard” porous	13.5	5.8	3.9	9.7	76.55
“Extra” porous	5.6	5.1	3.0	8.1	58.25

2.4. Detonation velocity test

The detonation velocity of ANFOs containing the three different grades of ammonium nitrate(V) was measured using an ionisation pin probe method. The ANFO charges were placed in glass tubes of 37/40 mm diameter and 700 mm length. The charges were initiated with an HC-14 detonator. Table 4 shows the test results.

Table 4. ANFO detonation velocity measurement results

Ammonium nitrate(V) grade in ANFO	Density [g/cm^3]	Detonation velocity [m/s]
Non-porous fertilizer	0.89	1850
“Standard” porous	0.84	1970
“Extra” porous	0.77	2640

3 Test result analysis

The smallest amounts of toxic oxides expressed as carbon monoxide equivalent were observed in the explosion products of ANFO containing “Extra” grade ammonium nitrate(V) (58.25 l/kg). ANFO containing the “Standard” grade generated a medium amount of toxic gases, between those containing fertiliser grade and the porous “Extra” grade (Table 3).

The high porosity of ammonium nitrate(V) determines its high absorption capacity and the ability to retain oil inside the granules (Table 1). Its porosity also affects the bulk density of different ANFO grades. Figures 6 and 7 shows the relationship between the concentrations and oil absorption capacity and bulk density of different grades used in the analysed ANFO samples to visualise the effect of physical parameters on the amount of hazardous oxides in post-explosion gases.

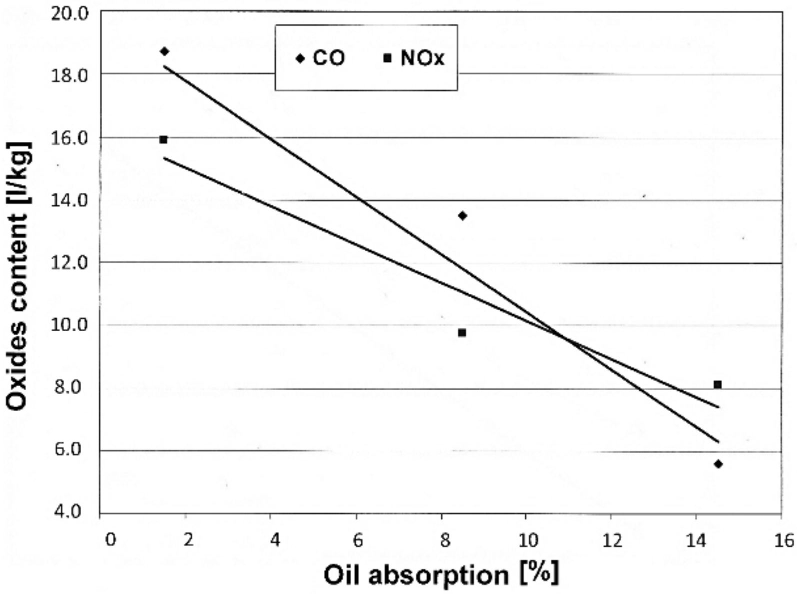

Figure 6. Relationship between the amount of nitrogen oxides in post-explosion gases and oil absorption capacity

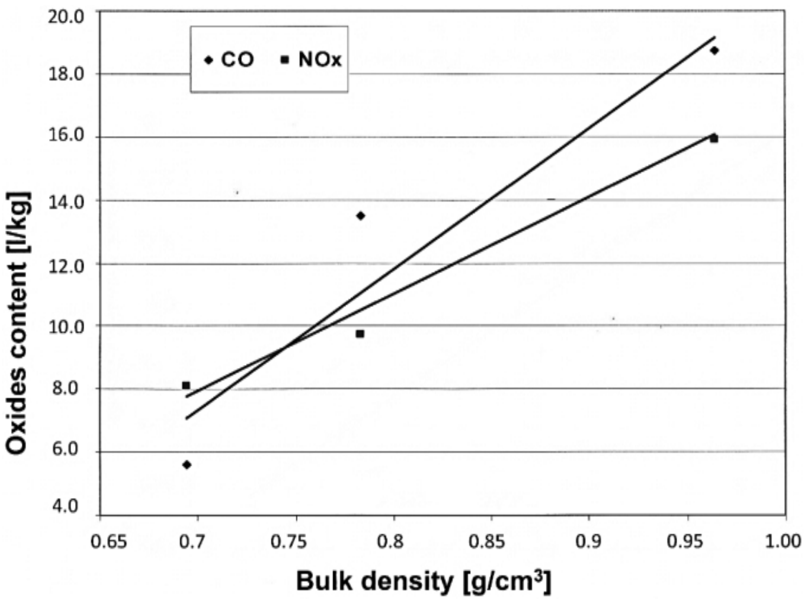

Figure 7. Relationship between the amount of nitrogen oxides in post-explosion gases and bulk density of ammonium nitrate(V)

The amount of toxic oxides (CO and NO_2) decreases with increases in oil absorption capacity of ammonium nitrate(V) (Figure 6) and a decrease in bulk density of the oxidising agent, determining the density of ANFO (Figure 7).

The highest detonation velocities were observed for the ANFO samples containing “Extra” grade porous ammonium nitrate(V) and the lowest for the samples containing the fertiliser grade. A significant difference was observed between the detonation velocities – 690 m/s (Table 4). A similar difference (~700 m/s) in detonation velocity of ANFOs containing ammonium nitrate(V) grades with an absorption capacity of 4 and 10 cm^3/100 g was also observed in the study [17]. A relatively low difference (120 m/s, Table 4) in detonation velocity of ANFO samples containing non-porous ammonium nitrate(V) and the porous “Standard” grade may be due to the fact that the fertiliser grade contains more fines (<1 mm) – 5.6% compared to 0.4% in the “Extra” grade – Table 1. One of the factors affecting the detonation velocity of ANFO samples is the particle size distribution of ammonium nitrate(V) [17]. Comparison of the detonation velocities of ANFO samples and the amount of generated toxic gases shows that the detonation velocity decreases with the amount of hazardous explosion products increasing.

4. Summary

- The study showed the significant effect of the physical and chemical properties of ammonium nitrate(V), depending on its morphology, on the amount of hazardous gases generated in the exothermic processes. An increase in the porosity of ammonium nitrate(V) resulted in a decrease in the amount of hazardous gases in the explosion products, since the substrate diffusion (mixing) process is the decisive factor for the reaction rate of explosive compositions (oxidiser-fuel) [21].
- The development of a specific surface area of ammonium nitrate(V) increases the area of chemical reaction between the products of exothermic decomposition of ammonium nitrate(V) and the products of endothermic oil pyrolysis. In the first stage of explosive reaction, the ammonium nitrate(V) is decomposed and the generated energy is used in the pyrolysis of the combustible compound. In the next stage, ANFO decomposition products react in a gaseous phase. The more the specific surface area of ammonium nitrate(V) granules develops the greater the intensity of chemical reaction, and the lower the amount of toxic oxides in the detonation products compared to ANFO samples containing non-porous ammonium nitrate(V).

References

[1] Maranda A., Cichosz Ł. Testing of Influence of Different Additives on Detonation Velocity of ANFO Explosives. (in Polish) *Mater. Wysokoenerg. (High Energy Mater.)* **2010**, *2*: 106-113.

[1] Maranda A. Paszula, J. Zawadzka-Małota I., Kuczyńska B., Witkowski W., Nikolczuk K., Wilk Z. Aluminum Powder Influence on ANFO Detonation Parameters. *Cent. Eur. J. Energ. Mater.* **2011**, *8*(4): 279-292.

[2] Maranda A., Nastała A., Buczkowski D., Witkowski W. Study of the Effect of Pesticides on Detonation Parameters ANFO and Ammonal Explosives. *CHEMIK* **2014**, *68*(1): 26-28.

[3] Biessikirski A., Ziąbka M., Dworzak M., Kuterasiński Ł., Twardosz M. Effect of Metal Addition on ANFO's Morphology and Energy Detonation. (in Polish) *Przem. Chem.* **2019**, *98*(6): 928-931.

[4] Araos M., Onederra I. Preliminary Detonation Study of Dry, Wet and Aluminized ANFO Using High-Speed Video. *Cent. Eur. J. Energ. Mater.* **2019**, *16*(2): 228-244.

[5] Dobrilović M., Škrlec V., Bohanek V. Velocity of Detonation of Low Density ANFO Mixture. *Proc. 16th Sem. New Trends Res. Energ. Mater.* Part II, Pardubice, Czech Republic, **2013**, 543-554.

[6] Dobrilović M., Bohanek V., Žganec S. Influence of Explosive Charge Temperature on the Velocity of Detonation of ANFO Explosives. *Cent. Eur. J. Energ. Mater*. **2014,** *11*(2): 191-197.

[7] Žganec S., Bohanek V., Dobrilović M. Influence of Primer on the Velocity Detonation of ANFO and Heavy ANFO Blends. *Cent. Eur. J. Energ. Mater.* **2016**, *13*(3): 695-705.

[8] Robbins D.L., Sheffield S.A., Dattelbaum D.M., Stahl D.B. Hugoniot and Properties of Diesel Fuel Used in ANFO. *Shock Compression of Condensed Matter – 2011. AIP Conf. Proc.* **2012**, *1426*: 828-831.

[9] Biessikirski A., Wądrzyk M., Janus R., Biegańska J., Jodłowski G., Kuterasiński Ł. Study of Fuel Oils Used in Ammonium Nitrate Based Explosives. (in Polish) *Przem. Chem.* **2018**, *97*(3): 457-462.
[10] Biessikirski A., Kuterasiński Ł. Morphological Properties of ANFO Explosives Obtained with Use of Liquid Combustibles. (in Polish) *Przem. Chem.* **2018**, *97*(4): 587-590.
[11] Biessikirski A., Kuterasiński Ł. Effect of the Alcohol Type Added to Ammonium Nitrate on the Structure and Morphology of Ammonium Nitrate-Based Explosives. (in Polish) *Przem. Chem.* **2018**, *97*(10): 1718-1721.
[12] Biessikirski A. Analysis of Morphological Properties of ANFO Explosives Based on Various Types of Ammonium Nitrate(V) and their Mixtures. (in Polish) *Przem. Chem.* **2018**, *97*(10): 1689-1692.
[13] Biessikirski A., Kuterasiński Ł., Pyra J., Dworzak M. Comparison of Properties of Ammonium Nitrates Used for Production of Fertilizers and Explosive Materials. (in Polish) *Przem. Chem.* **2016**, *95*(7): 1381-1384.
[14] Onederra I., Araos M. Blasting without Nitrogen Oxide Hazard. Alternative Explosives Developed. *CRC Mining News* **2015**. *30*: 05.
[15] Miyake A., Takahara K., Ogawa T., Ogata Y., Wada Y., Hiroyuki A. Influence of Physical Properties of Ammonium Nitrate on the Detonation Behaviour of ANFO. *J. Loss Prev. Proc. Ind.* **2001**, *14*: 533-538.
[16] Zygmunt B., Buczkowski D. Influence of Ammonium Nitrate Prills' on Detonation Velocity of ANFO. *Propellants Explos. Pyrotech.* **2007**, *32*(5): 411-414.
[17] Zawadzka-Małota I., Maranda A. Comparison of the Methods Used in Poland for the Determination of the Composition of Blasting Fumes after the Detonation of Mining Explosives. (in Polish) *Przegl. Gór.* **2008**, *65*(3): 27-32.
[18] Zawadzka-Małota I, Maranda A. Testing the Content of Toxic Components in Blasting Fumes According to the European Standard EN-13631-16:2002. (in Polish) *Conf. Proc. Blasting Techniques 2008*, Stara Leśna, Slovakia, **2008**, 23-29.
[19] Dubnov L.V., Bakharevich N.S., Romanov A.I. *Industrial Explosives.* (in Russian) Moskva: Izd. Nedra, **1973**.
[20] Maranda A. Analysis of Detonating Parameters and the Process Detonation of Mining Explosives. II. ANFOs. (in Polish) *Górn. Odkryw.* **2001**, *43*(5): 81-94.
[21] Maranda A., Gałęzowski D., Świetlik M. Research of Ammonium Nitrate Absorptivity Influence on Detonation Parameters of Mining ANFOs. (in Polish) *Przegl. Gór.* **1998**, *54*(11): 33-37.

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