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Comparison of structure, morphology, and topography of fertilizer-based explosives applied in the mining industry

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ABSTRACT

Samples of ANFO and an explosive matrix were studied using IR spectroscopy, X-ray diffraction, and scanning electron microscopy to compare their structure, morphology, along with topography.

IR and SEM analyses of ANFO showed that ammonium nitrate used for the manufacturing of this type of explosive has the same structure but different morphology, which is dependent on provenance.

The results of XRD, IR and SEM analyses for both tested samples of the emulsion explosive matrix have shown that its chemical composition has a major impact on their structure, morphology, and topography. The observed differences are due to the different composition of the dispersed phase and/or applied methodology during the preparation of the emulsion matrix.

1. Introduction

Ammonium nitrate (AN) is generally used either as a fertilizer or an ingredient of explosive material [1]. AN is effective fertilizer because of a high concentration of nitrogen (nearly 35.0%) and good solubility in water [2]. Depending on temperature AN solids exist under normal pressure in five stable polymorphic forms, which are designated as phases: I (ε -regular), II (δ –trigonal), III (γ-rhombic), IV (β-rhombic) and V (α-tetragonal) [3].

Transition temperature (°C)

- 17	32	84	125	170
Phase V ↔	Phase IV ↔	Phase III ↔	Phase II ↔	Phase I ↔ melt

The state of AN matter determines its application. AN prills used for manufacturing ANFO have lower density and higher porosity than fertilizer-grade AN, which leads to better absorption between the solid (AN) and liquid (fuel oil) phases. An aqueous solution of AN, by contrast, is used in the production of emulsion explosives or nitrous oxide [4,5].

Emulsion explosives are applied in the mining industry are usually water-in-oil emulsions, where the aqueous phase (an aqueous solution of AN) is dispersed in fuel oil. Moreover, emulsion explosives may contain minor amounts of other chemical compounds like urea, acetic acid or citric acid, which, during the production of the matrix, are responsible for obtaining the proper pH level. A low sensitivity to mechanical stimulus, an ability to regulate their density, water resistance and a low concentration of toxic oxides in post-shoot gasses allowed the applied emulsion explosives to become one of the most crucial exploding agents in the mining industry [6,7].

To produce emulsion explosives an aqueous solution of AN was used. A typical concentration of AN is ca 94.0 ÷ 99.0%. In the manufacturing of emulsion bulk explosives other various solutions like urea ammonium nitrate (UAN) may be used in the form of a supersaturated AN solution.

Numerous studies dedicated to explosives based on AN have been carried out. Wang and Fang [8] analyzed the influence of imide/amide emulsifier on the viscosity and visco-elastic properties of the emulsion matrix. They showed that matrixes with imide/amide emulsifier had higher viscosity at normal temperatures and better fluidity at high temperatures than the emulsion matrix based on a regular emulsifier. Xu et al. [9] made XRD, HRTEM and TG-MS analyses of ANFO samples containing Mn_2O_3 and Mn_2O_3/GO as additives. Moreover, they concluded that HNO_3 catalyzes AN thermal decomposition with a marked exothermic reaction. Němec [10] indicated that fortification and sensitization of the water-in-oil (W/O) emulsion explosive through the addition of demilitarized TNT could only provide acceptable results if the grain size of TNT did not exceed 400μm. Maranda et al. [11] tested $NaNO_2$ and MgH_2 as a new type of sensitizer and its effect on pressure changes and shock energy curves. In the case of ANFO, Paszula et al. [12] indicated that the detonation velocity of the AN/Al mixture

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decreased with increasing aluminum content, while Maranda et al. [13] examined AN and flaked aluminum morphology. Maranda et al. [13] concluded that an increase in the content of Al powder from 3.64 wt% to 12.12 wt% resulted in a two-fold decrease of the toxicity of the detonation products, increased work ability and enhanced the blast wave performance.

Maranda et al. discussed the emulsion explosive morphology in paper [5]. In his study Maranda et al. referred to emulsion explosives produced only based on the aqueous AN solution. The content of the AN in the AN solution was c.a. 93% (V/V). Properties of solid AN such as caking, rheology, morphology, friability, and the explosive characteristics of various ammonium nitrate prills were evaluated by Ramanarao et al. [14].

Studies shown in this paper supplement the current state-of-the-art topography, structure and morphology of ANFO and emulsion explosives, and present similarities and differences between explosives which are currently used in the mining industry and explosives which can be produced from various forms of mineral fertilizers. The researched ANFO was obtained based on ammonium nitrate porous prilled (AN-PP), which is applied in the mining industry, and AN-F, which is used as mineral fertilizer (in both cases AN in phase IV was studied). Explosive matrix (EM) samples were obtained from a 93.0% aqueous solution of AN, and from a urea AN solution (UAN) which is used in agriculture.

Topographical and morphological studies were conducted by infrared spectroscopy (IR), X-ray diffraction (XRD) and by scanning electron microscopy analyses (SEM).

2. Experimental

2.1. Materials

AN-PP was produced by Rostock division of Yara's International A SA. The grade of AN-PP was 35.0% nitrogen. The prill size range was 1–2 mm with a bulk density of 0.82 g·cm^{-3} at laboratory ambient conditions. The water content did not exceed 0.3%.

AN-F was produced by "Anwil" S.A. in Włocławek City. It contained 34.0% nitrogen, where 17.0% was in the form of nitrate nitrogen, 17.0% was in the form of ammoniacal nitrogen, and 0.2% magnesium in the form of magnesium nitrate. The prill size range was between 1 and 3 mm, and the bulk density was in the range of 0.92–1.0 g·cm^{-3}. The water content did not exceed 0.3%.

The ammonium nitrate solution was provided by Nitrogen Group Puławy Nitrogen Plant S.A. in Puławy City. It was based on a 93.0% of AN solution.

UAN was produced by Nitrogen Group Puławy Nitrogen Plant S.A. in Puławy City. It was in form of a clear, slightly yellowish liquid of a bulk density of 1.32 g·cm^{-3} at normal temperature and pressure. The UAN contained 32.0% of total nitrogen where 16.0% was in the form of ammoniacal nitrogen and nitrate nitrogen. The pH was ca. 7.0, and the max biuret content was ca. 0.5%.

2.2. Sample preparation

All ANFO samples were prepared by mixing AN-PP or AN-F with fuel oil in a weight ratio 94:6, and samples were blended for 20 min at 250 rpm in a mixer.

The emulsion matrix based on UAN (EM2) and the mixture of AN-PP with the UAN (EM3) were prepared in a laboratory. The scheme of the laboratory installation for the production of EM2 and EM3 is presented in Fig. 1.

The chemical composition of the EM2 is presented in Table 1. The UAN mixture was blended in the beaker (2) for 2 min at 500 rpm at 98.0 °C. After 2 min the mixture of fuel oil with sorbitan monooleate (emulsifier) was added from the flask (1) to the beaker (2). The blending of the mixture was further conducted at 1500 rpm at temperature 98.0 °C. The emulsification was observed at 11:00 min. The density of the matrix was 1.22 g/cm^3 and the viscosity at 20 °C was ca. 23,400 cP.

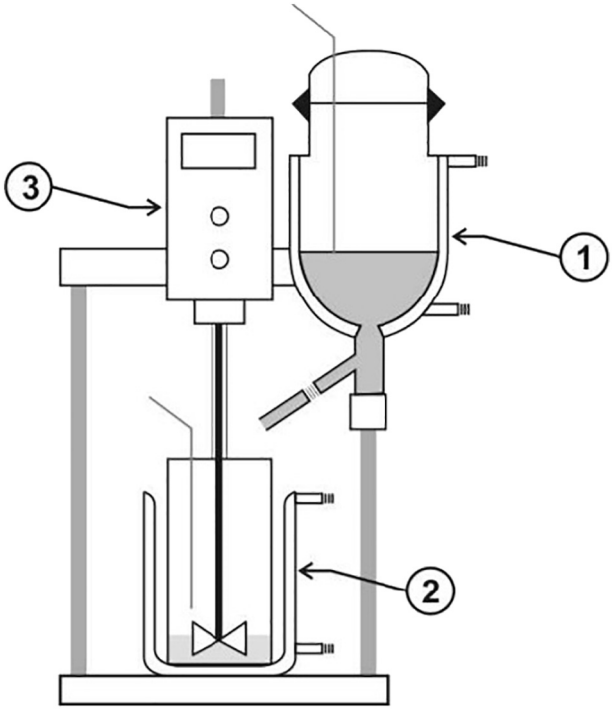

Fig. 1. Laboratory test stand for preparation of emulsion bulk explosives.
1 – Flask with UAN solution,
2 – Beaker with mixture of oil and emulsifier,
3 – Blender.

Table 1
Chemical composition of EM samples.

Sample	Content, wt%						
	AN solution	AN-PP	UAN	Water	Oil	Emulsifier	Others
EM1	78.5	–	–	14.8	4.8	1.7	0.2
EM2	–	–	78.5	15.0	4.8	1.7	–
EM3	–	31.2	52.3	10.0	4.8	1.7	–

The chemical composition of EM3 is presented in Table 1. AN-PP was blended with the UAN in the beaker (2) at 500 rpm at 98.0 °C. After AN-PP had changed its state of matter from solid to liquid the mixture of fuel oil with sorbitan monooleate (emulsifier) was added from the flask (1) to the beaker (2). The blending of the mixture was further conducted at 1500 rpm at 98.0 °C. The emulsification was observed at 3:50 min. The density of the matrix was 1.31 g/cm^3 and the viscosity at 20 °C was ca. 17,800 cP.

The chemical composition of the EM1 was presented in Table 1. The EM1 sample was tested by one of the blasting companies which operates on the Polish market. During the production of explosive matrix, additives such as acetic acid were provided in order to obtained a proper pH. The density of the EM1 was 1.28 g·cm^{-3} and the viscosity at 20 °C was ca. 55,000 cP.

During the low speed formation a coarse emulsion matrix of large polidispersed droplets was formed. A high-speed refining consisted of the subdivision of the droplets, so that the number of droplets exceeds the number of nucleation sites. Shakru et al. indicated that the emulsifier layered around the dispersed droplets in order to limit the crystal formation and the growth of the aqueous phase [15].