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Research paper

Modification of the Detonation Parameters of Mining Explosives Containing Hydrogen Peroxide and Aluminium Powder

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Abstract: Presently, due to rising environmental consciousness, numerous actions are being taken to prevent devastation of the natural environment. If explosive mixtures are manufactured in an insufficiently controlled manner, they contain too much ammonium nitrate and generate nitrogen oxides (NO_x), which are both harmful for living organism and responsible for negative weather phenomena. However, the products from decomposition of hydrogen peroxide are only oxygen and hydrogen, which are both environmentally friendly.
This paper presents the results of research on the impact of two types of aluminium powder on the detonation parameters of mining explosives containing hydrogen peroxide 60% as an oxidiser. The detonation velocities were measured by means of short circuit sensors. Direct measurement of the blast wave overpressure was performed with piezoelectric sensors and the positive phase impulse

was analyzed. Measurement of the explosive strength was made by the ballistic pendulum method for 10 g samples. The results of these experiments showed that the addition of both types of aluminium, as well as their content in the explosive mixture, have a significant impact on all of the measured parameters.

Keywords: hydrogen peroxide, detonation velocity, ammonium(V) nitrate, blast wave characteristics

1 Introduction

Explosives are a mixture of an oxidiser and fuel (reducer) material. In the case of mining explosives, the main oxidiser is ammonium nitrate (NH_4NO_3, AN). AN can be present in the following forms in explosives: comminute (ammonites, dynamites), porous (ANFO), aqueous saturated solution (slurry explosives), aqueous supersaturated solution (emulsion explosives).

In the last couple of years, work has been conducted using hydrogen peroxide (H_2O_2, HP) as the oxidiser instead of AN. This type of explosive contains no nitrogen atoms, and therefore the explosive had no possibility to produce fumes of nitrogen oxides (NO_x) after blasting, which is an environmental issue. Research on explosive mixtures containing HP began in the early 20th century. The first documented research was carried out in 1927 by Bamberger and Nussbaum [1]. They studied the following systems: HP (89 wt.% concentration)/cotton/vaseline of compositions 76/15/9 and 70/8.5/12.5. In the summary of their paper [1], the authors provided a commentary on the observed effects during high-energy transformations. Subsequently, in the years 1938-1944, experiments were carried out as part of a military programme entitled 'Research into explosives based on hydrogen peroxide' [2]. In this research, concentrated solutions of HP in the range of 61-100 wt.% were used, along with alcohols as fuels, and detonation velocities (VODs) of 6800-6300 m/s were obtained. The VOD decreased with explosives having a lower HP content.

After World War II, Shanley and Kaufmann worked with combinations of concentrated HP and glycerol, and a patent [2] was granted. In 1990 another patent was granted to Bouillet *et al.* [3], which used concentrated HP solution (>60 wt.%), organic combustible material and a gelling agents, in packaged products. Bouillet *et al.* [3] claimed VODs of about 7000 m/s, measured in PVC pipes, at a density of 1.20-1.38 g/cm^3. HP also detonates without fuels, as shown by the work by Sheffield *et* al. [4].

Currently, work on bulk explosives containing HP is being conducted in Australia by Araos and Onederra *et al.* [5-10]. The results obtained by the

Australian group motivated the establishment of a research program in Poland at the Institute of Industrial Organic Chemistry and the Military University of Technology [11, 12].

The aim of the group in Poland was to study the influence of Al powder, a common fuel in AN-based mining explosives, in combination with an explosive containing HP/AN – 90/10 ratio. This article reports the results of using two types of Al, in 3 different percentages (5, 10 and 15 wt.%), in the above mixture. Glycerine and guar gum were used to obtain a mixture with an oxygen balance close to zero.

2 Experimental Section

2.1 Characteristics of the raw materials used and the methodology of sample ME-HP preparation

For the preparation of mining explosives containing HP (ME-HP) the following substances were used in the tests:

- technically pure HP 60% w/w solution, (HP content: 58-60%, impurities (chlorides, phosphates, *etc.*): <0.2%) produced by Envolab (Poland) [13],
- AN (commercial grade: ≥98% AN, ≤2% magnesium nitrate, $MgNO_3$) Grupa Azoty Group Puławy S.A (Poland) [14],
- glycerine (pure, >98% glycerine, 0.00186% water) Eurochem BGP Sp. z o.o. (Poland),
- guar gum of SC-406 type (Meypradex),
- glass microspheres (MS) 3M type K-015 (experimentally determined bulk density 0.07 g/cm^3),
- Al powders produced by Benda-Lutz were used:
  - *i)* atomised Al BLS0052:AG45-90/99.7 ALATOMIZED:FU03 (Al_a) with a size distribution between 45-90 μm, bulk density 0.9 kg/l.
  - *ii)* flaked Al BLITZ ALUMINIUM DEPUVAL 3083 (Al_f) with an average particle size of 12 μm and maximum residue of 0.8% on a 45 μm sieve, and with a bulk density of 0.4 kg/l.

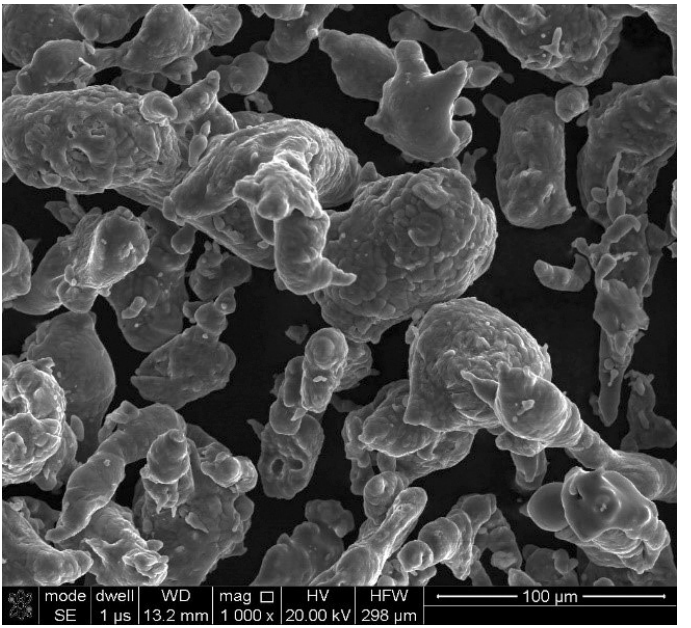
  Note that:
- Before commencing this work, a preliminary study was conducted in which HP and different metal powders were mixed. A temperature and volume increase in the sample was observed for the addition of an Al-Mg alloy powder during an observation period of 4 h. Therefore this material was dismissed from these studies and only Al_a and Al_f were selected for further study.

– Because mixtures of a very aggressive oxidant and metal powder could lead to uncontrolled reactions, HP with a relatively low concentration of 60% was used in this work.

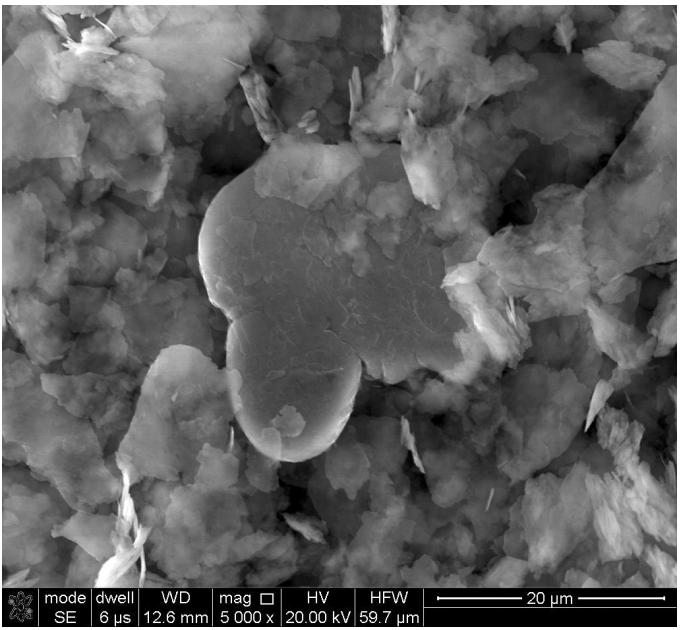
An elemental analysis on Al was carried out by scanning transmission electron microscopy (STEM) with HAADF and EDX technique. The results of the elemental compositions of the Al powders used are shown in Table 1. As seen, Al_f has about 1.4% less active metal than powder Al_a. This may slightly influence the results of the detonation parameters of the mixtures. Representative SEM images for the Al powders are shown in Figure 1.

Table 1. Elemental composition of the Al powders used [15]

Al powder	Element	Content [%]	
		mass	atomic
Al_f	oxygen	1.54	2.54
	Al	97.76	95.91
	carbon	0.70	1.55
Al_a	oxygen	0.47	0.78
	Al	99.2	99.48
	carbon	0.33	0.74



(a)



(b)

Figure 1. SEM micrographs of the Al powders used: Al_a (a) and Al_f (b)

The explosive samples (ME-HP) were prepared in the laboratory. The composition of the matrix for the tests is shown in Table 2. The matrix was prepared by dosing individual components into the mixer. In the first stage ground AN (grain size <0.8 mm) was poured, then HP was added. After preliminary mixing, the mixture of glycerine and guar gum was added. Test samples were obtained by the introduction of Al powder and glass microspheres (MS) into the matrix. After further intensive mixing, a homogeneous mixture was obtained. After the addition of each of these components, the sample was thoroughly mixed. The final stage of homogenisation was carried out very gently, due to the low mechanical strength of the MS. On completion, the density of the ME-HP was measured.

Table 2. The composition of the test matrix

Component	Content [wt.%]
HP (60 wt.%)	73.0
AN	10.0
Glycerine	14.0
Guar gum	3.0

2.2 Research methodology

The following parameters for the ME-HP samples were measured:

– density,
– VOD,
– blast wave overpressure,
– explosive strength.

The densities of the test samples were measured by repeatedly filling and weighing a cylinder of known volume.

The VODs of the explosive samples were measured by means of short circuit sensors. Samples were placed in PVC pipes with the inner/outer diameters of 45/50 mm and length of about 22 cm, depending on the density. All of the tested samples had the same weight, 400 g. There were four short-circuit sensors along the pipes. The last sensor was placed at a distance of 15 mm from the bottom of the charge, and the others were located at 40 mm intervals. The charges were initiated by an electric detonator type "ERG" (primer #8), and a 10 g booster of pressed phlegmatized 1,3,5-trinitro-1,3,5-triazinane (RDX).

Direct measurement of the incident blast wave overpressure was performed with piezoelectric sensors from Piezotronics (PCB sensors 137A22 and 137A24). The measuring system consisted of 4 piezoelectric sensors placed on a metal frame. Two of them were placed 2.0 m away from the charge, and the other two were 2.5 m away. The device recording the pressure readings was a four-channel oscilloscope. The charge was suspended 1.5 m above the ground and 1.0 m away from a wall opposite to the sensors. The measurements of VOD and blast wave overpressure were recorded simultaneously. A schematic of the arrangement is displayed in Figure 2.

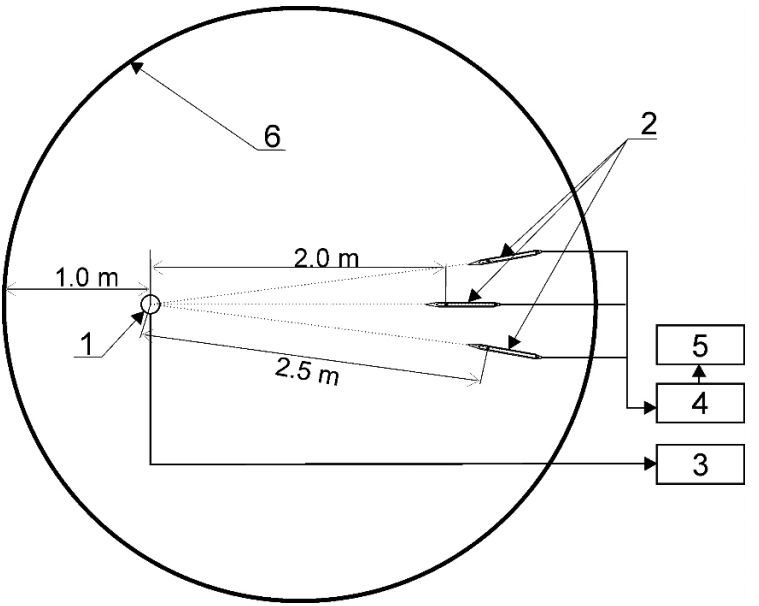


Figure 2. Scheme of the measuring system: 1 – explosive charge, 2 – pencil probes, 3 – time meter, 4 – signal conditioner, 5 – oscilloscope, 6 – bunker wall

The blast wave overpressures obtained by this method are characterised by high irregularity, which may be caused by disturbances from the electric grid or the measurement line (as a result of system vibrations) and as a result of impacts of shrapnel created by detonation on the sensor. These factors lead to waveforms containing a large number of disturbances in the form of peaks – points significantly deviating from the actual measurement points. That is why the results obtained in the study have been smoothed out, among other things, by removing these disturbances, as this does not significantly affect the values obtained, as well as by using an appropriate approximation to standardise the waveform. In this study, the approximation of the overpressure changes with time was performed using the modified Friedlander equation. Two or three tests were performed for each explosive composition and the mean values of the detonation velocity, blast wave overpressure and impulse were determined. The mean deviation was also determined for these values.

The measurement of explosive strength was made using the ballistic pendulum method for 10 g samples. Three tests were performed for each explosive. The charges were initiated with an ERG detonator. A 10 g RDX charge with a density of 1 g/cm^3 was used as reference.

3 Results and Discussion

3.1 Density

A curve of % MS content in the ME-HP mixture *vs.* resulting density was constructed. The results are shown in Figure 3. The calculated uncertainty of these measurements was about 0.4%. ME-HP samples containing 1.00% of MS were used for further testing.

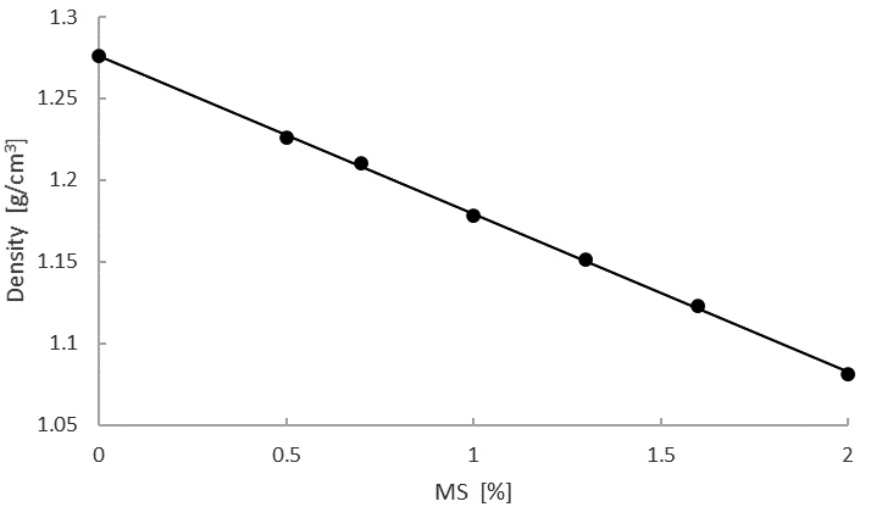


Figure 3. Dependence of the density of the explosive mixture on the MS content

Charges containing 5, 10 and 15% Al powder were prepared immediately before firing. Before commencing the tests of the detonation parameters, the sample densities were measured. These results are presented in Table 3. The mixtures containing 5-10% of Al powder have an oxygen balance closest to zero.

Table 3. Densities of the explosive materials as a function of Al content

Composition of explosives [wt.%]				Oxygen balance [%]	Density (±0.01) [g/cm^3]
Type of Al	ME-HP	MS	Al		
Al_a	99.00	1.00	–	+6.81	1.18
	94.05	0.95	5.00	+2.03	1.26
	89.10	0.90	10.00	–2.76	1.30
	84.15	0.85	15.00	–7.54	1.32
Al_f	99.00	1.00	–	+6.81	1.18
	94.05	0.95	5.00	+2.03	1.10
	89.10	0.90	10.00	–2.76	1.01
	84.15	0.85	15.00	–7.54	0.92

3.2 VOD

The change in density of the tested explosive samples influences the measured VOD. Therefore various methods are undertaken to determine the effect of the Al addition. One of the methods is to perform the test with the addition of LiF instead of Al [16, 17]. Another possible method is to use the experimental correction presented by Cooper [18]. This method was used, for example, in the work of Manner *et al.* [17]. Equation 1 was used to calculate the corrected VOD.

$$D_c = D_e + x(\rho_c - \rho_e) \tag{1}$$

where D_c is the corrected VOD, D_e is the experimental VOD, ρ_c and ρ_e are the corrected and experimental densities, respectively, x is the experimental coefficient. In [18] it was suggested that $x = 3$, which for many explosives is a fair average over a small density range (10-15%). The results of the experimental and corrected VODs for individual ME-HP mixtures, depending on the content and type of Al powder used, are shown in Figure 4.

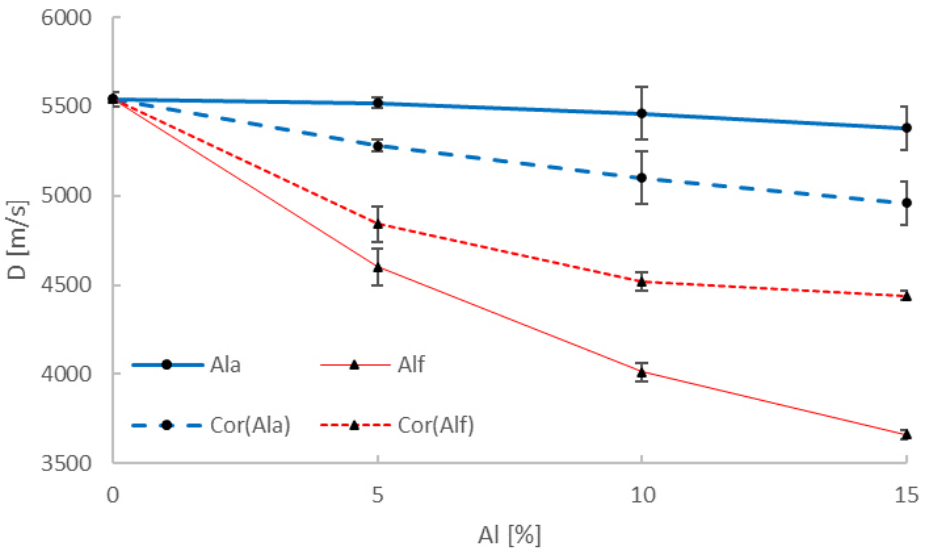


Figure 4. The dependence of the experimental and corrected VOD on the content and type of Al powder used

It may be observed that in the case of ME-HP, the introduction of Al powder into the tested mixture results in a decrease in the corrected VOD. With the increase in Al_f content, there is a much larger decrease in the VOD than for Al_a addition. One of the factors that can contribute to a much higher decrease of the VOD for Al_f is the much lower density of ME-HPs containing Al_f compared to mixtures with the same content of Al_a. The tested MEs behaved similarly to emulsion explosives, for which the VOD decreases with increasing Al content [15]. This behaviour may result from heat absorption by the Al powder in the reaction zone of the detonation wave.

3.3 Blast wave overpressure

Figure 5 shows examples of blast wave overpressure patterns obtained during these tests. Table 4 lists the maximum overpressures and positive phase pulses of the blast waves. For sensors at a distance of 2.5 m, the overpressure of the blast wave after the addition of Al powder increased until the Al powder content was 10%, for both Al_a and Al_f, and then decreased (Table 4). In the case of charges with Al_f and sensors at a distance of 2.0 m, the overpressure appeared to be constant, within experimental error, over the whole Al_f range. Higher overpressure values were observed for Al_a. The highest overpressure value was obtained for mixtures containing 10% of Al_a. On the other hand, the positive

phase impulse of the blast wave for both types of Al powder increased with increasing amounts of Al, reaching the highest values for 15% Al (Table 4), but the differences were very slight.

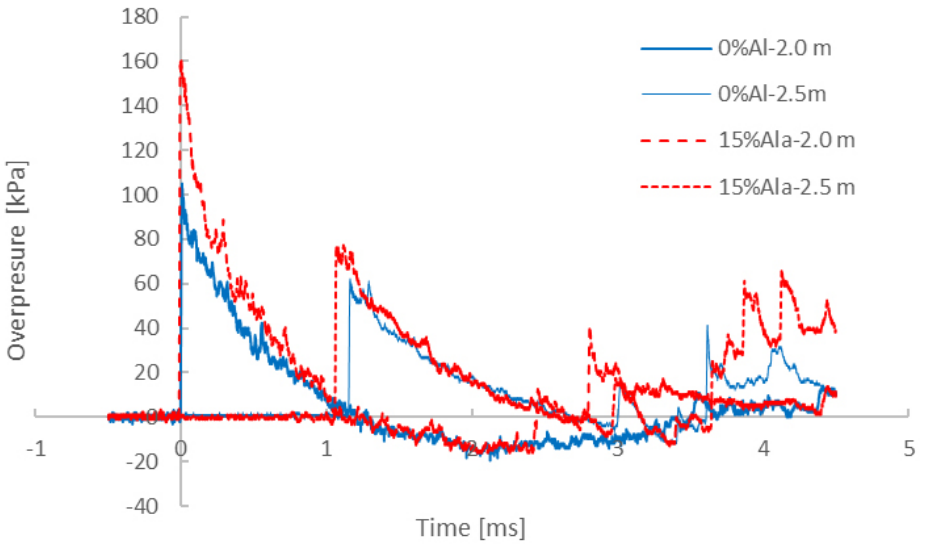


Figure 5. Blast wave overpressure for the tested materials, without addition of Al powder and with the addition of 15% Al_a

Table 4. Dependence of maximum blast wave overpressure and positive phase impulse on the content and type of Al powder (sensors were placed 2.0 and 2.5 m from the explosive charge)

Al powder		Sensors at distance of [m]			
		2.0		2.5	
Type	Content [%]	Overpressure [kPa]	Impulse [Pa·s]	Overpressure [kPa]	Impulse [Pa·s]
Al_a	0	96 ±5	42 ±2	41 ±1	28 ±1
	5	111 ±3	47 ±1	60 ±4	31 ±2
	10	122 ±1	49 ±2	68 ±2	34 ±1
	15	118 ±7	51 ±1	64 ±5	38 ±1
Al_f	0	96 ±5	42 ±2	41 ±1	28 ±1
	5	93 ±5	37 ±1	56 ±4	28 ±2
	10	92 ±4	37 ±2	60 ±5	31 ±1
	15	90 ±11	43 ±5	50 ±5	34 ±2

3.4 Ballistic pendulum method

During the final experimental stage, the power (ability to do work) of the investigated explosives was measured using the ballistic pendulum method. The mean values and the mean deviation of the explosive strength for the tested mixtures are summarised in Table 5. The relative ability of the tested explosive mixtures to do work, determined by means of the ballistic pendulum method, increased with the amount of Al powder (Table 5). Higher values of this parameter, with the same content of the metallic additive, were obtained for ME-HP containing Al_a powder, *i.e.* analogous to the measurements of the parameters of the blast waves.

Table 5. Measurement of explosive strength based on the ballistic pendulum method

Al powder		Power of explosive [% *vs* RDX]
Type	Content [%]	
Al_a	0	65 ±5
	5	74 ±4
	10	84 ±4
	15	85 ±4
Al_f	0	65 ±5
	5	70 ±4
	10	75 ±4
	15	79 ±4

4 Conclusions

- A series of explosives based on HP with a concentration of 60 wt.% with the addition of different amounts of two types of Al powder, atomised (Al_a) and flaked (Al_f), were investigated. The VOD, blast wave parameters and the strength of the tested explosives were measured. The results of these experiments showed that the addition of both types of Al has a significant impact on all of the measured parameters.
- For mixtures of the ME-HP matrix with the addition of various amounts of glass microspheres, a linear decrease in density was found with an increase in the microsphere content. The mixture of the ME-HP matrix with the addition of 1% glass microspheres was selected for further tests.

- For the selected mixture, the density increased with increasing Al_a content but decreased with increasing Al_f content. The significant decrease in density for mixtures with the addition of Al_f is probably due to the high specific surface area of Al_f. The addition of such a powder to the explosives probably causes the introduction of additional air bubbles, lowering its density, however further research is required to determine the amount of air bubbles and their influence on the density of the tested mixtures.
- The VOD decreased with increased amounts of Al_f and Al_a additives. The decrease was higher for the mixture with Al_f. The decrease in the VOD may result primarily from a decrease in the density of the mixture. It can be concluded that for Al_f, the detonation parameters are significantly reduced as a result of heat absorption by the powder in the reaction zone of the detonation wave. In the case of Al_a, the heat absorption is lower due to the larger particle diameter.
- The highest value of the air blast wave overpressure was obtained with 10% Al_a. An increase in the positive phase impulse was found for the addition of both types of Al powder. As the distance from the charge increases, the difference between the blast wave impulse for the mixtures with Al_a and Al_f is decreased. This phenomenon may suggest that the greater fineness of the Al_f may be conducive to longer after-burning of Al behind the detonation wave.
- The relative ability to perform work, as determined by the ballistic pendulum method, is higher for ME-HP containing Al_a.
- Varying the grinding of the Al powder used in the experiments has an impact on the differences in the behaviour of the metallic additive during detonation of the tested mixtures. The Al_f powder has a larger specific surface area and smaller grains than Al_a. Addition of the former powder to the mixture causes a decrease in density and a stronger absorption of heat by the Al_f in the zone of chemical reaction of the detonation wave, and the detonation parameters are lowered more.

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