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Review / Przegląd

Properties of explosive systems containing water
Właściwości wybuchowych układów zawierających wodę

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Abstract: *The paper presents the of the properties of explosive mixtures containing water as one of the basic components. The literature data analysis was performed for binary mixtures containing: aluminum dust, ammonium nitrate(V) and high-energy explosives (nitrocellulose, trinitrotoluene, hexogene, pentrite) or their mixtures, smokeless powders in addition to water. The most frequently described parameters were the brisance, the detonation velocity and the detonation capacity.*

Streszczenie: *W artykule przedstawiono właściwości wybuchowych mieszanin zawierających wodę jako podstawowy składnik. Analizę danych literaturowych wykonano dla mieszanin binarnych zawierających oprócz wody: pył aluminiowy, azotan(V) amonu lub wysokoenergetyczne materiały wybuchowe (trinitrotoluen, heksogen, pentryt) lub ich mieszaniny oraz prochy bezdymne. Najczęściej opisanymi parametrami były: kruszność, prędkość detonacji i zdolność do detonacji.*

Keywords: *water, high explosives, aluminium dust, ammonium nitrate(V), brisance, detonation velocity, detonation capacity*

Słowa kluczowe: *woda, materiały wybuchowe kruszące, pył aluminiowy, azotan(V) amonu, kruszność, prędkość detonacji, zdolność do detonacji*

1. Introduction

Explosives used in military technology and the mining industry are usually mixtures, the components of which are characterized by different physical and chemical properties. The diversity of these properties causes them to play a varied role affecting the structure of the explosive composition and its detonation parameters. One of the unusual additives to explosives is water. A chemically inert substance that does not make a positive contribution to the heat of explosion, and therefore potentially reduces the detonation parameters of the explosives, but allows to form its unusual structure. This paper presents the effect of water on detonation parameters of different explosive systems.

2. Water-aluminum dust system (WAS)

The first binary water systems contained aluminum dust as a second component. In 1946, Shidlovskiy investigated the explosive properties of stoichiometric mixtures of aluminum dust with water (or methanol) and magnesium dust with water (or methanol) [1-3]. The aim of the research was to create by detonation, the oxides of the tested metals. A partial explosive reaction for mixtures of aluminum dust (grain size ~ 0.595 mm) with water gelatin thickened to 4%,was obtained in the Hess test. The charge mass of the tested explosive mixture was 50 g, initiated by a tetryl detonator, caused complete deformation of the lead cylinder, as well as unreacted aluminum residue being observed [1, 3].

Shidlovskiy's research was continued in 1951 by Medard [2-4]. Similarly to Shidlovskiy, he conducted experiments with stoichiometric H_2O-Al compositions, in which he used fine aluminum dust <105 µm. The mixtures, in cylinders of 35 mm diameter, 4 mm thick and 390 mm long, were initiated with a pentrite/mononitronaphthalene 95/5 detonator (mass of 50 g). A full detonation process did not occur. In the next test, Medard mixed H_2O-Al sensitized with various amounts of pentrite until he obtained a full detonation of the whole charge.

The detonation velocity of the explosives containing more than 7% pentrite was about 3000 m/s. He also compared the obtained mixture to TNT as part of the *sand test*. Similar ground crater dimensions were obtained for the tested explosives of 2500 and 880 g TNT. As in the Hess test performed by Shidłovskiy, Medard found remains of unreacted aluminum dust in the crater [2, 4]. The explosive mixtures developed by Shidlovskiy and Medard did not find a practical application.

The concept of explosives consisting of a mixture of water and aluminum dust returned after fifty years. The ALICE rocket fuel (acronym for the chemical symbol of aluminum Al and the word: ice) was developed, containing a stoichiometric mixture of water and aluminum dust of nanometric grain size [5-11], which was cooled below the freezing point of water. In order to determine their safety, impact and initial sensitivity tests were performed [12]. The tested mixtures contained five types of nanometric aluminum dust with average grain sizes of 38, 70, 80, 100 and 100-200 nm and the content of active aluminum, respectively: 54.3%, 74.0%, 79.0%, 86.0% and 86.1%. Rocket fuel samples were cooled to –30 °C. As part of the impact sensitivity measurements, 50 mg of ALICE rocket fuel samples were placed on sandpaper and loaded with a 5 kg hammer impact falling from various heights. The tested samples did not ignite up to the height of 2.2 m from which the hammer fell, which is the maximum for the BAM fall hammer used. Experiments to determine sensitivity to initiation, using the *small-scale zero gap test method* [13], consisted of placing 3 g of the rocket fuel in a hole passing through an entire cooled (-30 °C) aluminum block, located on a metal plate. The charge was initiated with 3 g of a plastic explosive based on pentrite. A positive test result – a 0.46 mm deep cavity in the control plate - was found only for rocket fuel containing nanometric aluminum dust with an average size of 38 nm. The test result can be explained by two factors. The smallest dimensions of the nanometric aluminum dust and the lowest density of the rocket fuel samples which contained it i.e. 42% of the theoretical density. In comparison, samples made from nanometric aluminum dust with a grain size of 80 nm had an average of ≈80% of the theoretical density [12].

3. Water – ammonium nitrate(V) (AN) system (WANS)

Aqueous concentrated solutions of AN are an intermediate used in the production of emulsion explosives. In order to determine their potential explosive properties, which may pose a hazard during their manufacturing, detonation capability and detonation velocity were investigated [14]. The experiments were conducted in steel pipes with an inner diameter of 6 inches, insulated with a ceramic jacket. Inside the pipe there was a heating element allowing the AN solutions to be heated in the range of 127-152 °C. The density of the solutions was reduced to values of 0.8, 1.0 and 1.2 g/cm^3 by several minutes aeration. The pH of the solutions was varied and adjusted by the addition of nitric acid(V). Charges were initiated with a 454 g booster of plastic explosive C-4. Nineteen experiments were carried out and in five it was found that a detonation process had occured. The results of the positive trials, which were obtained only with AN solutions with a density of 0.8 g/cm^3 , are shown in Table 1 and Figure 1.

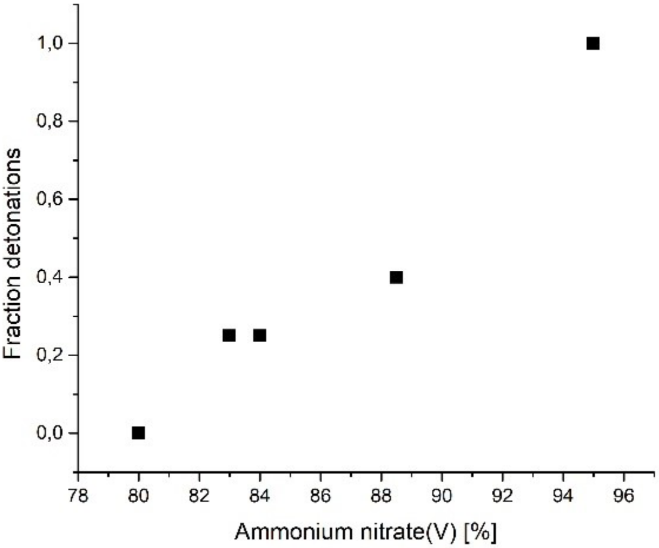

Figure. 1. Dependence of the detonation incident fraction on the concentration of AN solutions with density of 0.8 g/cm^3 [14]

Table 1. Results of detonation velocity measurements of AN solutions [14]

Concentration of aqueous solution of AN [%]	pH of the solution	Temperature [°C]	Detonation velocity [m/s]
83.0	2.5	126.9	2180
84.0	~8	144.4	2280
88.5	2.0	151.9	2280
88.5	~8	150.4	2470
95.0	~2.5	152.4	2040

The results show that even at relatively low concentrations (83.0%) of aqueous solution, air bubbles cause sensitization. The authors of the paper do not provide the size of the gaseous inclusions, but believe that these are larger than typical sensitizers of emulsion explosives - glass microspheres or plastic microballoons. However, it should be said that during the process of obtaining emulsions, gases other than air may be included, also with a smaller bubble size and with higher sensitizing ability. So the results obtained in this paper are not directly applicable. A surprisingly low detonation velocity was obtained for the highest tested concentration of solution, which does not correlate completely with data for lower concentrations and has no theoretical explanation [14].

4. Water-solid explosive systems (WSES)

In 1874, Abel [15-17] found that the detonation velocity of wet nitrocellulose (containing 15-30% water) was higher than that of dry nitrocellulose. He reported the following values for:

- dry nitrocellulose: 5320 m/s,
- nitrocellulose with 15% of water: 6095 m/s,
- nitrocellulose with 30% of water: 5960 m/s.

This was confirmed by Kast [16, 18, 19], showing an increase in the detonation velocity of nitrocellulose after the addition of water, from 6300 m/s (for dry pressed nitrocellulose with a density of 1.30 g/cm^3) to 6800 m/s (for pressed containing 16% water). The ability of the above-mentioned nitrocelluloses to perform work with the water addition, decreased from 375 to 280 cm^3 [16, 19]. The given experimental data concerning detonation velocity of moist nitrocellulose, resulted in charges based on this material, being widely used for many years. For example, in the Russian army in the 19th century, artillery shells were developed with nitrocellulose containing 20% water. During World War II, the British Army used sapper cubes made of moist nitrocellulose. In the years 1943-1945, Sytiy, using water-saturated nitrocellulose in blasting works, found that compared with dry nitrocellulose better blasting of rock mass and granite fragmentation was obtained than with dry nitrocellulose [17, 20].

The lack of general data on the effect addition of non-explosive liquids has on the detonation velocity of solid explosives was the main reason for Urbański and Galas carrying out a wide range of studies on this subject in 1939 [21]. Detonation velocity tests were performed using the Dautriche method in 20/26 mm steel tubes. The tested composition densities were 1.45 g/cm^3 for hexogen and pentrite and 1.45 g/cm^3 for TNT. In order to avoid dissolution of the solid explosives tested, their temperature was in the range of –5 to +5 °C. The experimental results, which included the detonation velocities of TNT, hexogen and pentrite mixtures also with water, supplemented with a physico-chemical interpretation, were presented by Urbanski after 33 years, in his work [16] (see Table 2).

Table 2. Water content effect on detonation velocity of solid explosives [16]

Type of explosive	**Water content [%]**						
	0	5	10	15	20	25	30
Pentrite	7295	7259	7445	–	7130	–	6645
Hexogen	7705	–	7235	–	7775	–	7070
TNT	6625	5820	5795	5715	5915	5670	–

Two cycles of experiments were carried out by Apin, determining comparatively the brisance of solid explosives and their mixtures with water [17]. In the first series of experiments, he studied charges containing microporous and crystalline TNT. An additional issue was the grain size of TNT. The results of the experiments are summarized in Table 3.

Table 3. TNT brisance depending on the size and structure of the TNT grains [17]

TNT type	**Water content [%]**	**Density [g/cm^3]**	**Brisance [mm], grain size [mm]**			
			4-2.3	2.3-1.3	1.3-0.4	<0.4
Microporous	0.0 34.0	0.83 1.26	5.5 22.6	8.5 21.3	16.5 22.6	19.0 21.4
Crystalline	0.0 35.1	0.83 1.28	6.5 0.8	3.4 0.9	16.0 1.0	19.0 0.8

The next experiments involved smokeless powders (nitroglycerine and nitrocellulose). The variables were the shape of the powder grains, their dimensions and water content. Results of the measurements are shown in Table 4.

Table 4. Water effect on the brisance of smokeless powders [17]

Powder type	Grain size [mm]	Water content [%]	Density [g/cm$^{3]}$	Brisance [mm]
Nitroglycerine	d = 2.9; l = 3.0	28.6	1.30	0.4
		0.0	0.93	3.0
	d = 0.4; l = 3.0	37.5	1.28	0.6
		0.0	0.80	14.0
	1.0×1.0×0.15*$^{)}$	33.3	1.25	2.2
		0.0	0.83	22.0
Nitrocellulose	d = 0.8/1,5**$^{)}$; l = 7.5	36.7	1.26	22.2
		0.0	0.80	2.4
	d = 0.2/0.9; l = 1.5	28.6	1.33	24.0
		0.0	0.80	13.5

** – square flakes 0.15 mm thick, **– single-hole powder*

In opencast mining, blasting is very often carried out in unstable holes. Typical mining explosives containing AN with different liquid fuels (amonites) are not water-resistant explosives. Therefore, before slurry explosives and later emulsion explosives were developed, in many countries granulated explosives were used in water holes [22]. The main component was TNT, characterized by its minimal solubility in water - 0.15% at 100 °C. In the Soviet Union, two granular waterproof explosives called granulotoles (TNT) and alumotoles (TNT containing 15% of aluminum dust) were used. Their parameters in dry form and those containing 30% of water, are shown in Table 5.

Table 5. Parameters of explosives known as granulotol and alumotol [23]

Parameter	Granulotol		Alumotol	
	Dry	Wet	Dry	Wet
Heat of explosion [kcal/kg]	825-870	1000	1130-1260	1340
Volume of gaseous explosion products [l/kg]	745	895	635	815
The ability to perform work:				
– Trauzl block [ml]	285-295	320	420-440	–
– Ballistic pendulum (compared to TNT)	1.00	1.13	1.10	1.30
Density [g/cm^3]:				
– bulk	0.95-1.00	–	0.95-1.00	–
– granules	1.48-1.54	–	1.52-1.68	–
Brisance (Hess test) [mm]	24-26	32-34	28-30	TD*$^{)}$
Critical diameter (mm), type of charge:				
– without cover	60-80	–	70-80	–
– with cover	–	5-10	–	5-10
Detonation velocity [km/s]	4.5-5.0	5.5-6.7	4.3-8.0	5.5-6.0

** TD – total destruction of lead cylinder*

Complementary to the experiments on dry and wet TNT, results of the measurements concerning the influence of the TNT form on the brisance by the Hess method, are summarized in Table 6.

Table 6. Influence of TNT form on brisance [23, 24]

Parameter	TNT		
	Milled	**Flaked**	**Granulated**
Bulk density [g/cm^3]	1.00	0.73	0.90
Crushability [mm]:			
– dry	16	7-14	10-12
– wet	ND*)	6-13	21-23

** ND – no detonation*

From the data summarized in Table 6, it can be seen that the highest degree of transformation was obtained for the wet granular TNT. On the other hand, the greatest phlegmatic effect of water was observed for those charges containing wet milled TNT. Therefore, in blasting works, spherical shaped pellets of granulotol and alumotol had diameters of about 5 mm [23]. In another work [25], milled hexogen was also found to have a significant effect on the critical diameter of the wet form.

The study of the effect of water on the parameters of explosives crushing was continued in the late 1970s and early 1980s by Zygmunt [26-28], and most of the experimental results can also be found in the monograph [29]. The experiments included hexolite (TNT and hexogen) 50/50. Hexogen grain size used in the experiments was less than 63 μm. The obtained hexolite granules were divided into seven sieve fractions and the critical diameter was determined for dry and water-filled charges (Figure 2).

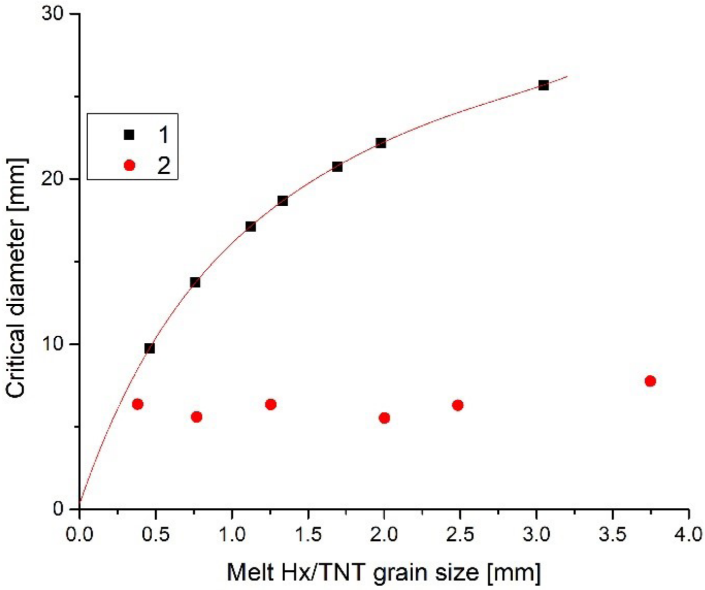

Figure 2. Dependence of critical diameter of granular hexolite on grain size. Horizontal segments indicate the range of sieve fraction: 1 – dry granules, 2 – mixture of granules with water [27, 29]

Zygmunt [27, 29] measured the critical diameter for the 1.0-2.5 mm hexolite sieve fraction as a function of hexogen content and granulation temperature of the TNT/Hx 50/50 mixture. The experimental results obtained are illustrated in Figures 3 and 4.

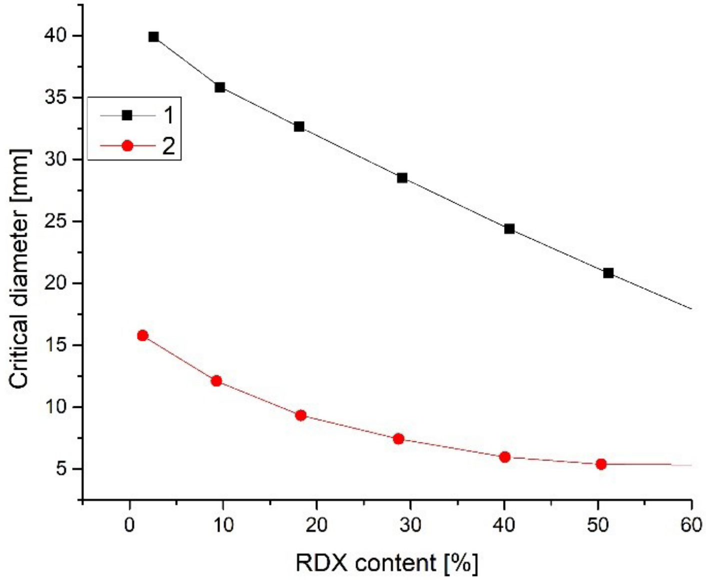

Figure 3. Dependence of critical diameter of granulated hexolite on hexogen content: 1 – dry granules, 2 – mixture of granules with water [27, 29]

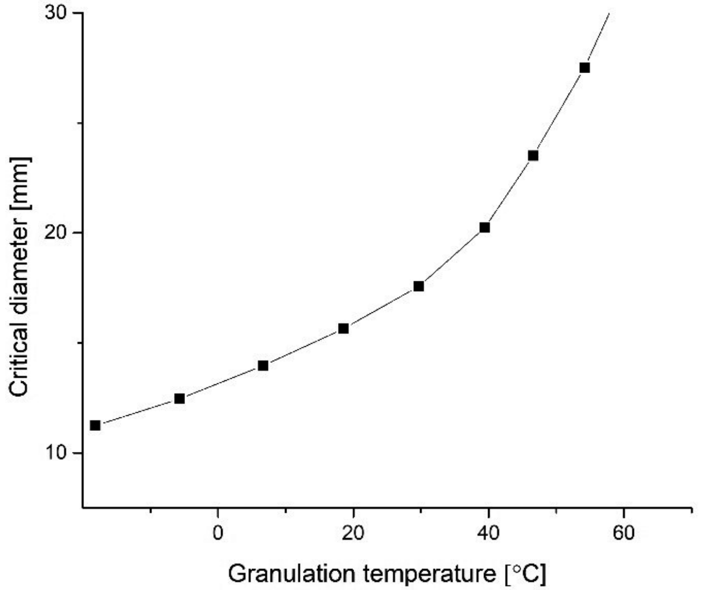

Figure 4. Dependence of critical diameter of 50/50 hexolite on granulation temperature [27, 29]

Zygmunt [27, 29] also compared critical diameters (Figure 5) and detonation velocities (Figure 6) for hexolite 50/50 (grain size specified in Figures 5 and 6 description), pentrite (grain size 0.2-0.5 mm) and hexogen (grain size 0.1-0.3 mm). For pentrite and hexolite, he carried out measurements in 18 mm diameter tubes and for hexogen in tubes of 30 mm diameter.

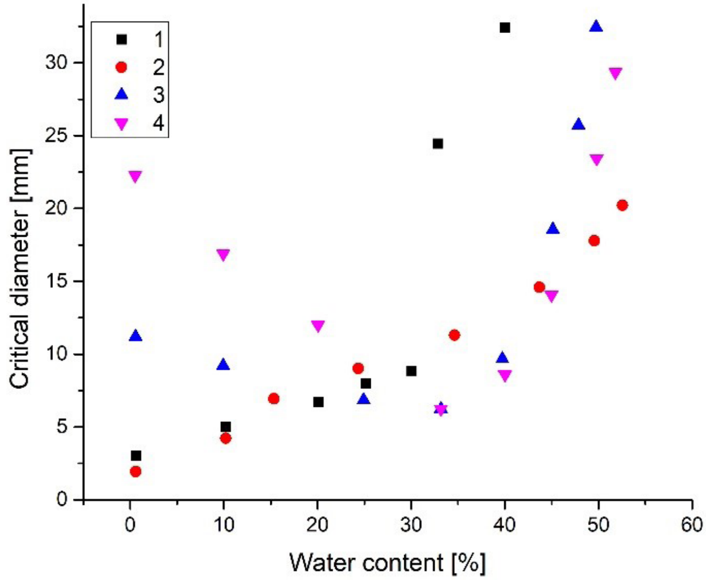

Figure 5. Dependence of critical diameter of explosive-water mixtures on water content [27, 29]: 1 – Hx, 2 – PETN, 3 – hexolite (1.5-2.5 mm), 4 – hexolite (0.2-0.5 mm)

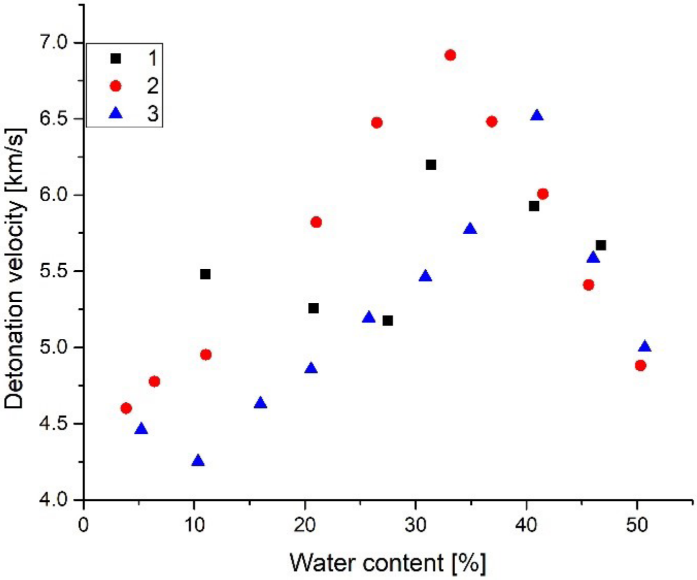

Figure 6. Dependence of detonation velocity of explosive-water mixtures on water content [27, 29]: 1 – Hx, 2 – PETN, 3 – hexolite (0.5-1.0 mm)

Zygmunt [27, 29], similarly to Urbanski [16], analyzed the experimental results very carefully. Unlike Urbanski, his research included another very important detonation parameter besides the detonation velocity – the critical diameter. He assumed that two factors cause a change in the detonation parameters of explosives-water systems:

- decrease of initiation connected level to the extinction of „hot spots”,
- improvement of shock wave propagation conditions due to the displacement of air by the liquid [29].

Reduction in the „hot spots” concentration and „hot spots” efficiency cause the increase in critical diameter. In the case of grains of low homogeneity (hexolites), an increase in water content to 33% causes a decrease in the critical diameter, associated with increasing the effectiveness of „hot spots”. Above this concentration, an increase in the critical diameter is observed because the phlegmatizing water effect rules – explosive grains stop touching, and the distance between them begins to increase (Figure 6).

However, for homogeneous crystals of pentrite and hexogen, the addition of water has an exclusively phlegmatising effect. A water content of 33% for hexogen is characteristic, from which a sharp increase of the critical diameter occurs (Figure 6). In the case of pentrite, there was an increase in critical diameter with increasing water content according to the Zygmunt research (Figure 6), which is directly related to the higher detonation capacity of pentrite relative to hexogen. The minimum shock wave pressure capable of initiating detonation of hexogen is 17 GPa (ρ_o = 1.80 g/cm^3) and for pentrite is 11 GPa (ρ_o = 1.70 g/cm^3) [22, 30].

Zygmunt believes that air displacement increases the density of the explosive system. He also points out that for the analyzed explosive systems, non-ideal detonation velocity is actually measured. So in the range of diameters below the limit, where the obtained values of the measured parameter are influenced by e.g: the structure and disintegration of the grains. The character of dependence of detonation velocity on water content is a result of two tendencies:

- increase of detonation velocity related to the increase of density of the system,
- increase or decrease of this parameter due to decrease or increase of the critical diameter.

In the case of hexolites these tendencies are compatible. Up to a water content of 33% (total replacement of air by water) there is an increase in the detonation velocity resulting from an increase in the density of the mixture and a decrease in the critical diameter. Above this content, there is a decrease in the detonation velocity, determined by a decrease in the density of the system (density of hexolites is higher than water) and an increase in the critical diameter. In the case of hexogen and pentrite in the range of water content up to 33%, both tendencies are opposite, which results in a minimum on the curve $D = f(\%H_2O)$ – Figure 5.

Solid explosives were used in the Polish mining industry after the political and economic transformation of the early 1990s. This was due to a low supply of mining explosives and a lot of explosives from military stocks and decommissioned ammunition. TNT (pelletized and flaked), pressed hexogen-based charges, and nitrocellulose powder were used mostly in open-mining holes [31, 32].

5. Conclusions

- ♦ The binary systems described contain components which differ in physical and chemical parameters, which directly affect their explosive performance. The water-aluminum dust system acquires the ability to detonate only after the addition of a few percent of pentrite, an explosive material which is characterized by very high sensitivity to mechanical stimuli and a low critical diameter. Before the addition of pentrite, there are no „hot spots” in this system, which constitute the conditions for propagation of the detonation wave. The second solution to sensitization is by reduction of the material density, for example by adding a nanometric dust along with air, whose microbubbles occluded on the metal surface, creating „hot spots”. From the point of view of the potential use of ALICE as a rocket fuel, the lack of detonation capability is definitely an advantage.
- ♦ In a water-aluminum dust system, water plays an unusual role by being an oxidizer of the metal. ALICE rocket fuels, in the initial stage of preparation, have a consistency similar to toothpaste [33]. This is related to the addition of thickener to the liquid, to prevent the aluminum dust from sedimentation. The fuel is then placed in a mould and cooled -30 °C for 24 h before ignition. In 2009, a test was conducted at Scholer University Purdue in Indiana with a 3-meter rocket which soared to a height of 1,300 feet. Dr. Steven F. Son, a research team member from Purdue, said [33]: „ALICE can be improved

with the addition of oxidizers and become a potential solid rocket propellant on Earth. Theoretically, ALICE can be manufactured in distant places like the Moon or Mars, instead of being transported to distant locations at high cost”. ALICE rocket fuel is considered to be an environmentally friendly rocket propulsion system because the gaseous product of combustion is hydrogen [34].

- The water-AN system attains characterized with explosive properties after intense aeration (with a decrease in density to 0.8-1.0 g/cm^3), and thus after the formation of „hot spots”. AN solutions are the main component of slurry explosives [35] and emulsion explosives [36]. Slurry explosives were divided into two types by Cook [37]: slurry blasting agents and slurry explosives. Slurry blasting agents (SBA) do not contain high-explosives and one of the solutions is to sensitize them by the addition of flaked aluminum dust, e.g. [38, 39]. Along with the metallic additive, air is introduced into the SBA matrix, forming „hot spots” on the surface of the aluminum dust flakes, so the sensitization process is analogous to the process which occurs in ALICE rocket fuel.
- The third water-solid explosive system is part of the slurry explosives. The explosive properties of this system depends, as was to be expected, on its water content, among other things. Water addition, to a known value, in the case of nitrocellulose, hexogen, pentrite, hexolite (Figure 6), granulatol and alumotol (Table 5) caused an increase in detonation velocity. Also, the addition of water leads to an increase in the crushability of nitrocellulose powder (Table 4), granulotol, alumotol (Table 5) and microporous TNT (Table 3) and a decrease in this parameter for nitroglycerin-based powder (Table 4) and crystalline TNT (Table 3). The deciding factor affecting the crushability value of water-TNT systems is determined by the particle size of the explosive component. WSES containing TNT with larger grains have higher crushability (Table 6). The addition of water affects the detonation capacity of WSES in different ways. It causes an increase in the critical diameter of pentrite and hexogen and a decrease in the case of hexolite within a certain range of liquid component content (Figure 5).
- The results of the study of the explosive parameters of water-containing systems presented above can be said to have „historical” value only, since in general, slurry explosives in which WSES components are the basic component, are no longer use in the mining industry. However, nitrocellulose gunpowder has found application in emulsion explosives, and its effect on EE parameters was described in a paper [40]. Also, research on various forms of EE sensitization are still being continued, e.g. [41-48] and knowledge of WANS properties can help with their interpretation.

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