Analysis of selected parameters of saletrols and emulsion explosives

Ramona SITKIEWICZ-WOŁODKO, Andrzej MARANDA* – Department of Explosives, Faculty of Advanced Technologies and Chemistry, Military Academy of Technology, Warsaw, Poland

Introduction

Development of mining explosives (ME) is connected with modification of functional forms of ammoniac saltpeter (AS). It is used in particulate form (ammonites, karbonites, metanit, dynamites, barbaryts), granular form (saletrols), saturated aqueous solution (suspension explosives) or supersaturated aqueous solution (emulsion explosives). Nowadays, the most popular mining explosives are ANFOs (saletrols) and emulsion explosives. Amount of explosives used in industry in Poland has increased significantly. In 2004 total explosive consumption was: 10,035,973 kg, and in 2013 – 37,642,694 kg [1]. Consumption of emulsion explosives and ANFO-type explosives in underground and open-pit mines is presented in Table 1. Increase in emulsion explosive application is especially pronounced, as their use in Polish open-pit mining industry was in 2004: 34.7%, and in 2013 – 43.6%.

Table 1

Consumption of explosives in mines in the years 2009–2013 [2]

Year	Explosive, kg	
	Saletrols	**Emulsion explosives**
2009	8,737,938	19,032,914
2010	8,623,477	20,683,608
2011	11,364,684	24,497,504
2012	18,898,015	21,683,689
2013	7,028,406	23,512,587

Emulsion explosives and ANFO-type materials due to their advantages are of special interest for many research teams working on development of innovative blasting agents. Despite the fact that they have been known for dozens of years, scientific journals still publish new results of experiments and numerical estimations of their properties. Authors present in this paper a subjective selection of the most important papers published in the years 2010–2014.

Saletrols

Saletrols containing granulated ammoniac saltpeter have been patented in 1955 in the US. This marks beginning of research involving mainly selection of appropriate liquid fuel, modification of structure of ammoniac saltpeter granules and increasing their water-resistance. Although first variations of saletrols were developed in 1850s, the listed above fields of research resulted in that some of them can be considered state-of-the-art explosives. This is true mainly for saletrols containing highly porous ammoniac saltpetre. The importance of this property of ammoniac saltpetre, as well as dominant role of innovative variations of saletrols in open-pit mining industry is proven by publications presented in the recent years on important conference on mining explosives and blasting technique.

By appropriate processing operations, ammoniac saltpeter of developed external and internal surface area can be obtained. Structure of ammoniac saltpetre granules next to effect on saletrol physicochemical properties determines their detonability and value of detonation parameters – detonation rate and working ability [3].

Effect of various factors on saletrol detonation parameters

Porosity of ammoniac saltpetre plays important role for efficiency of ANFO-type explosives on rock mass blasting. Ammonium nitrate (V) density at 25°C is 1.66 g/cm^3 [1]. Ammonium saltpetre granules are of 1.4–1.5 g/cm^3 density, while their bulk density is 0.75–0.85 g/cm^3. Texture of porous ammoniac saltpetre contains external and internal pores. Outer porosity provides absorption ability of such amount of organic fuel into ammoniac saltpetre granules that allows obtaining mixtures of maximum thermodynamic and detonation parameters. This also formation of physically stable and macroscopically homogeneous explosive mixture that can be transported on long distances and has extended storage time. While internal porosity is a basic factor determining final density of explosive mixture. Internal pores play role of "hotspots" that determine initiation of chemical reactions that become detonation.

Tests of detonation parameters of saletrols can be found in papers [4 – 7]. In article [4] detonation rate of saletrol (ammonium nitrate (V)/oil 94.6/5 of density 0.823 g/cm^3) in steel pipes 55/65 mm using reference detonators containing: 0.25 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g of pentryt as initiators. Measurements were conducted on four distances (100 mm each). On the last measurement section for pentryt mass of 0.25 g, 956 m/s was obtained, while for 1.0 g –2,353 m/s. As shown by experimental results, it may be concluded that the greater pentryr mass in the detonator, the greater detonation rate. Bohanek *et al.* [4] when using pentryt detonators as initiators of mass: 20 g, 50 g, 100 g, have also obtained detonation rates increasing with detonator mass: 3,043 m/s, 3,205 m/s and 3,456 m/s, respectively.
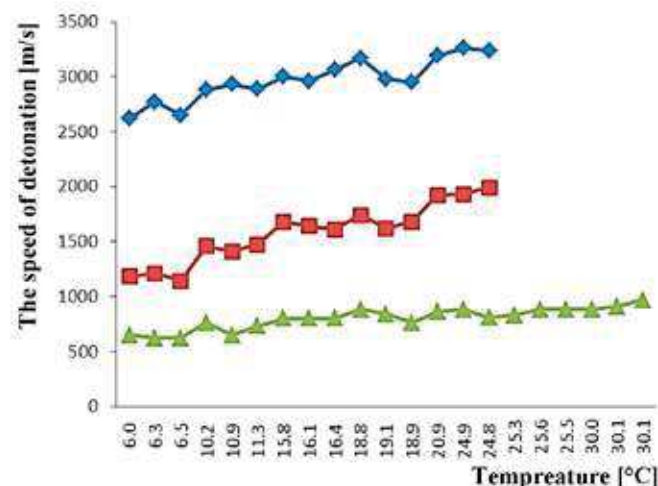

Fig. 1. Temperature effect on detonation rate of saletrol charge:♦ – pipe 52/57 mm, detonator ▪ – pipe 52/57 mm, fuse, ▲ – pipe 23.5/27.5 mm, fuse, [5]

Studies [5] conducted for saletrol charges (ammonium nitrate (V)/oil 94./5.5, density 0.823 g/cm^3) placed in steel pipes of diameter 52/57 mm and 23.5/27.5 mm and for different initiators (electric fuse containing 0.72 g of pentryt, detonator of specified mass of explosives) has found that as temperature increases, detonation rate increases as well. Type of initiator has also effect on the measured parameter (Fig. 1).

Some blasting techniques use saletrols of reduced detonation parameters that can be achieved by using material of low bulk density as a component. The paper [6] involves use of expanded polystyrene of grain size in range of 1.5–3.5 mm and bulk density of 0.019 g/cm^3 as a density reducing agent for heavy-ANFO (mixture of saletrol and emulsion explosive matrix). Saletrol contained 94.4% of ammonium nitrate (V) and 5.6% of oil, while emulsion explosive matrix had the following composition: oxidisers – 80.07%, organic phase – 5.73%, water – 14.20%. Saletrol/ emulsion explosive matrix volume ratio was 90/10. Detonation rate measurements were carried out was mixtures containing various amounts of expanded polystyrene in steel pipes of inner diameter of 20 mm and outer diameter of 150 mm. The experiment results are presented in Table 2.

Table 2

Detonation rates for mixtures of heavy-ANFO with polystyrene [6]

Explosive	Volume ratio	Density g/cm^3	Detonation rate m/s
(ANFO+matrix)/polystyrene	90/10	0.801	1999
(ANFO+matrix)/polystyrene	80/20	0.714	1777
(ANFO+matrix)/polystyrene	70/30	0.628	1602
(ANFO+matrix)/polystyrene	60/40	0.541	1562
(ANFO+matrix)/polystyrene	50/50	0.454	1520
(ANFO+matrix)/polystyrene	40/60	0.367	1260
(ANFO+matrix)/polystyrene	30/70	0.280	804
(ANFO+matrix)/polystyrene	20/80	0.193	524

The obtained results show monotonic decrease of detonation rate of tested mixtures as density decreases – expanded polystyrene content increases. Polystyrene not only decreases the density, but also shifts oxygen balance of explosive mixtures towards negative values, having unfavourable effect on thermodynamic parameters.

Effect of aluminium powder addition on detonation parameters and harmful component content in saletrol explosion products

Detonation of explosive results in formation of large amounts of gaseous explosion products. Some of them, mainly carbon monoxide and nitrogen oxides are harmful to health of miners present in the area of blasting operations, as well as have negative environmental impact. Therefore, studies are conducted to test content of toxic ingredients emitted during detonation for explosives used in underground mines. The Central Mining Institute in cooperation with the Military University of Technology and the Institute of Industrial Organic Chemistry (IPO) conducted studies on effect of aluminium powder on concentration of toxic post-explosion gases [8]. Experiments were conducted for aluminized saletrols of oxygen balance close to zero, of composition presented in Table 3.

Table 3

Compositions of tested aluminized saletrols [8]

Ingredients, %	Explosive		
	ANFO-Al-1	ANFO-Al-2	ANFO-Al-3
Porous NH$_4$NO$_3$	91.85	88.71	85.23
Flaked aluminium powder	3.64	7.27	12.12
Oil FLEX401	4.51	4.02	2.65

In order to expose micromorphology of tested ammoniac saltpetre samples, internal and external structure was studied by means of SEM. Ammoniac saltpetre sample structure is presented in Figure 2. Tested ammoniac saltpetre is of porous structure with multiple openings visible in SEM images. Granules are of regular spherical shape with diameter of approx. 1 mm with pore size of ~50 μm. Absorptivity for oil FLEX 401 was up to approx. 9.5% of weight.
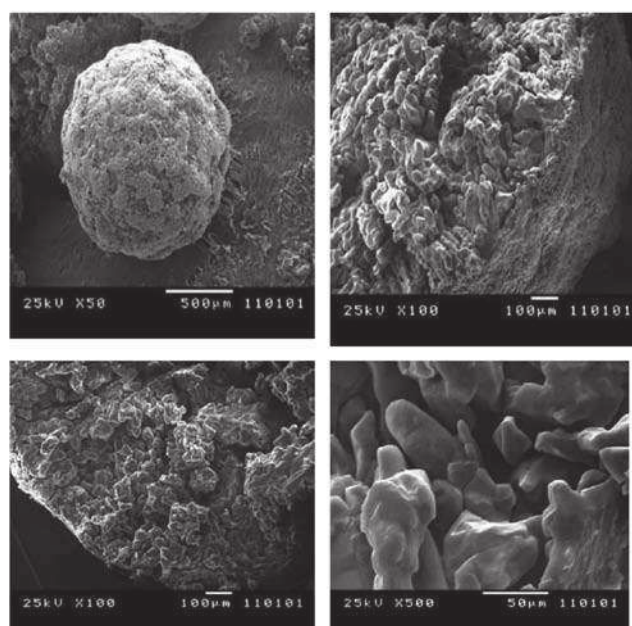
Fig. 2. Microstructure of ammoniac saltpetre of "Extra" type [8]

Test results of toxic gas content in saletrol explosion products are summarized in Table 4.

Table 4

Effect of flaked aluminium powder content on concentration of toxic explosion products [8]

Ingredient	Explosive		
	ANFO-Al-1	ANFO-Al-2	ANFO-Al-3
	Content, l/kg		
CO	5.53	8.67	7.43
NO	5.22	3.75	0.93
NO$_2$	2.17	1.69	0.47
NO$_x$	7.39	5.45	1.40
CO+NO$_x$	20.31	19.56	10.23

Increase in flaked aluminium powder content from 3.64% to 12.12% caused double drop in concentration of toxic explosion products. This is a result of the fact that increase of aluminium powder quantity results in temperature increase in chemical reaction zone due to the high heat of combustion for aluminium, which allows greater conversion of ingredients of explosive mixture.

The paper [8] presents also results of working ability of aluminized saletrols measured using Held method (Fig. 3).
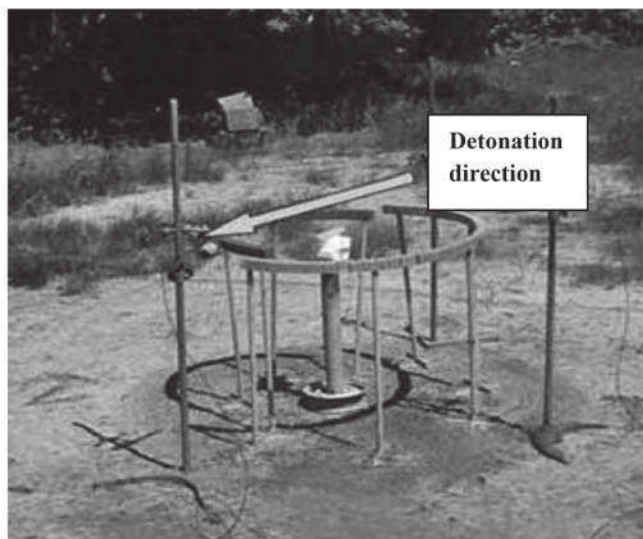

Fig. 3. Test station for Held test [8]

Table 5 presents maximum and averaged values of density pulse obtained for three types of saletrols. Density pulse ID was determined using the formula

$$I_D = I/A = (m \cdot V)/A = (F \cdot t)/A \qquad (1)$$

where:
I – pulse, kg·m/s
A – surface area of driven block, cm²
F – force, N
m – block weight, kg
V – velocity, m/s
t – time, s

Table 5

Maximum and average values of density pulse for tested ANFO-Al [8]

Explosive	Diameter 0.5 m, steel block				Diameter 0.75 m, aluminium block			
	I_D, 10^5 Pa·s		I_{Ds}, 10^5 Pa·s/kg $^{-1/3}$		I_D, 10^5 Pa·s		I_{Ds}, 10^5 Pa·s/kg $^{-1/3}$	
	Max.	Average	Max.	Average	Max.	Average	Max.	Average
ANFO-Al 1	1.06 E-002	3.82 E-003	1.44 E-002	5.19 E-003	6.86 E-003	2.35 E-003	9.31 E-003	3.18 E-003
ANFO-Al 2	8.43 E-003	3.60 E-003	1.14 E-002	4.88 E-003	6.64 E-003	2.75 E-003	9.02 E-003	3.69 E-003
ANFO-Al 3	1.16 E-002	3.95 E-003	1.58 E-002	5.36 E-003	7.47 E-003	2.96 E-003	1.01 E-002	4.02 E-003

Data (Tab. 5) shows that increase of flaked aluminium powder content increases density pulse, thus increasing working capability of saletrols. By changing aluminium powder content one can adjust thermodynamic parameters of saletrols adopting them to the mechanical properties of the exploited rock mass.

Emulsion explosives

Main ingredients of emulsion explosives are: oxidisers, fuels, water, emulsifiers, sensitisers and modifiers. Ammonium, alkali metals and alkaline earth metals nitrates (V), chlorates (V) and chlorates (VII) are used as oxidisers. Ammonium nitrate(V) is most often used, also as a mixture with sodium or calcium nitrate(V). Oxidiser content in

emulsion explosives reaches almost 90%. Fuels used in emulsion explosives can be divided into 3 groups:
– organic liquids forming solutions with water,
– organic liquids not forming solutions with water,
– solid fuels such as coal, sulphur, aluminium powder of various grain size, milled cereal seeds; they are used as additional fuels and their content in emulsion explosives can be up to 15% [3].

Water is a very important texture-creating agent of emulsion explosives. Its content depends on the type of used emulsifier and affects significantly their detonability, density and explosion properties. Emulsion explosives are based on emulsion of "water in oil" type, called matrix. The matrix has density of approx. 1.4 g/cm³. It has no explosive properties, therefore it has to be sensitized in order to obtain explosive material. To that end, high-energy explosives are added to the matrix, or gas bubbles serving as so-called hotspots are formed mechanically or chemically.

Large number of publications [9 – 28] shows continuous high interest in emulsion explosives in the last years despite the fact that first versions of these explosives were developed in 1969 [1]. Main directions of the research involve emulsion explosive matrix stability [9 – 12] and basic detonation parameters of emulsion explosives [13 – 29].

Matrix stability

Stability of explosives can be defined as an ability to maintain invariable physical and chemical properties for a long time. Physical stability depends on properties of components of explosive mixtures as well as on the stability of the structure they form. Mining explosives in comparison with explosives used in military have relatively low stability. This property is determined among others by hygroscopicity of main component of mining explosives, i.e. ammonium nitrate (V). In case of emulsion explosives, there may occur processes causing changes particularly in their structure (emulsion inversion leading to crystallisation of oxidisers) that will have direct negative impact on their detonation parameters, especially on detonability. The results of conducted studies show that high stability of emulsion explosive matrix can be obtained when such conditions as the following are maintained: selection of proper emulsifier or mixture of emulsifier (polymer-based emulsifiers increase stability), using high-quality components of organic phase, using pure substances in non-continuous phase, appropriate regime of technological process, correct sensitization method appropriate for emulsion explosive application method [12].

The paper [13] presents studies on effect of Fe[(NO$_3$)$_4$]$^-$ ions on thermal stability of ammonium nitrate (V) and emulsion explosives. It was found that iron (III) nitrate (V) has catalytic properties that reduce initial decomposition temperature of ammonium nitrate and emulsion explosive matrix (V) by 60.16°C and 30.33°C, respectively. Critical temperature of emulsion explosives in the presence of Fe[(NO$_3$)$_4$]$^-$ ion was decreased even by up to 22.6% (Tab. 6).

Table 6

Initial decomposition temperature of pure nitrate (V) and emulsion explosive matrix and with addition of iron (III) nitrate (V) and ammonium chloride by means of ARC [13]

No.	Sample	Weight g	Temperature °C
1	Ammonium nitrate(V)	0.497	241.066
2	Ammonium nitrate(V)/iron(III) nitrate(V)	0.496	180.911
3	Ammonium nitrate(V)/ammonium chloride	0.501	181.033
4	Emulsion explosive matrix	0.200	241.18
5	EE matrix/iron(III) nitrate(V)	0.200	210.85
6	EE matrix/ammonium chloride	0.210	230.75

Detonation rate and working ability

One of the parameters, most often described in the literature is detonation rate that can be defined as rate of propagation of chemical reaction zone in detonating explosive. Their characteristic properties are stationarity and maximum dimensions under given conditions. Detonation rate for given explosive is not a constant value. Explosive detonation rate may be greatly affected by the following factors: charge density, diameter and envelope, fineness of crystals and, for mixtures, component content and composition structure. Another very important parameter is working capability that determines efficiency of rock mass blasting or degree of fermentation of missile shell.

Density effect on denotation parameters of emulsion explosives was studied in [14]. Density of matrix composed of: ammonium nitrate (V) – 64.4%, sodium nitrate (V) – 14.6%, organic phase – 6.0% and water – 15.0% was controlled by addition of microballoons 092 DE 120 30. Increase in sensitizer content from 0.6% to 3.4% caused decrease in density in range 1.07–0.55 g/cm^3, which resulted in decrease in detonation rate measured in pipes of 50 mm diameter from 4,870 m/s to 3,110 m/s and was particularly pronounced in the first stage of density reduction.

Comparative tests were conducted involving effect of addition of glass microballoons (HGMB), polymer microballoons (HPMB) [15] on detonation rate and pressure of emulsion explosives. Results of the conducted studies are presented in Figure 4, while Figure 5 illustrates dependence of detonation rate on porosity, which is defined by the following equation:

$$\Phi = (\rho_M - \rho_o)/(\rho_M - \rho_{MB}) \qquad (2)$$

where:
ρ_M – matrix density,
ρ_o – emulsion explosive density,
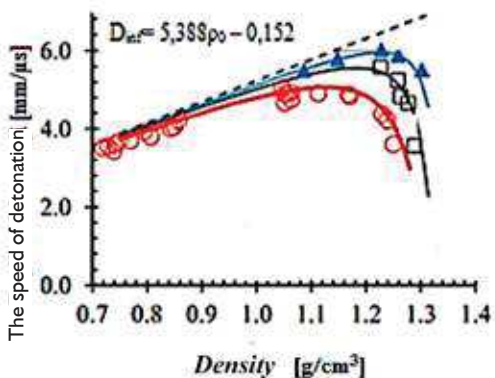$\qquad \rho_{MB}$ – sensitizer density.

a
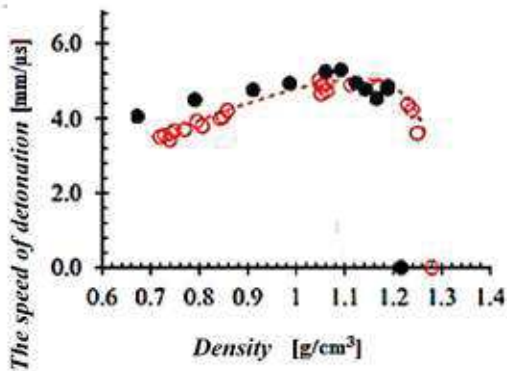
b

Fig. 4. Effect of density on detonation rate of emulsion explosives sensitized with: A) ○ – HGMB, • – HPMB, B) EE sensitized with HGMB of charge diameter: ○ – 25 mm, □ – 52 mm, ▲ – 102.5 mm [15]
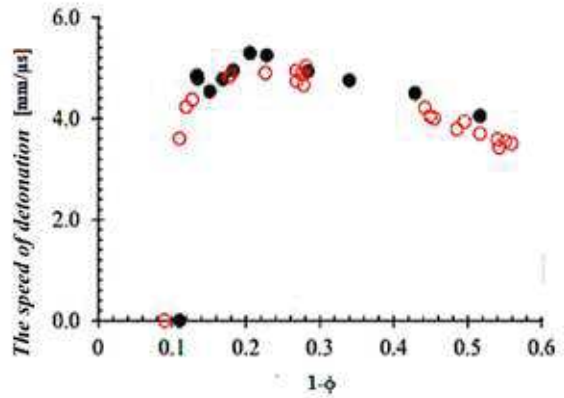

Fig. 5. Detonation rate of EEs sensitized with ○ – HGMB, • – HPMB as a function of 1-Φ [15]

Figure 6 presents comparison of excess pressure profiles measured for emulsion explosives sensitized with glass microspheres of various porosities.
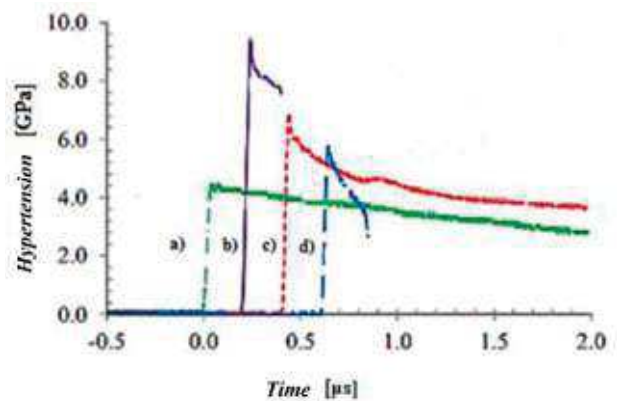

Fig. 6. Excess pressure profile for EEs sensitized with HGMB for various porosities: a) 0.12, b) 0.25, c) 0.39, d) 0.51 [15]

Detonation rate of EEs sensitized with HMBP increases linearly as charge density increases and is higher than detonation rates of EEs sensitized with HGMB. Moreover, porosity is very important here. As charge porosity increases, the denotation rate decreases both for EEs sensitized with HGMB and HPMB. Critical density, at which detonation decays corresponds to porosity of 0.11 and 0.09, respectively.

The tested emulsion explosives very physically sensitized by addition of glass or polymer microspheres. Other form of sensitization can be chemical foaming, that can be achieved by adding magnesium hydride to emulsion explosive matrix that undergoes decomposition therein, which leads to generation of hydrogen microbubbles [16, 17]. Paper [16] presents comparative studies of the EEs of matrix composed of: ammonium nitrate(V) – 75%; sodium nitrate (V) – 10%, organic phase – 7%, water – 8%. Three types of sensitizers were used: glass microspheres, mixture of glass microspheres and aluminium powder, magnesium hydride. EEs compositions and experimentally determined and theoretically estimated explosion heats are summarized in Table 7.

Table 7

Composition and explosion heat [16]

Matrix, %	Sensitizer, %			Explosion heat, kJ/kg	
	Glass microsphere	Al	H$_2$Mg	experimental	theoretical
100	4	-	-	2728	3297
	4	4	-	3028	3684
	-	-	2	3574	3530

For the presented mixtures (Tab. 7) detonation rates were measured. Experiments were conducted in 48.5/50.5 mm plastic pipes. Moreover, measurements of brisance using Hess method (sample weight 50 g) and sensitivity to mechanical stimuli. Test results are presented in Table 8.

Parameters of emulsion explosives sensitized with various substances [16]

| Type of sensitizer	Density g/cm³	Detonation rate m/s	Brisance mm	Friction sensitivity N	Temperature resistance K
Glass microsphere	1.21	4434	16.1	>358	>503
Glass microsphe-res/Al	1.24	4389	16.2	>358	>503
H₂Mg	1.29	5552	19.1	>358	>503

Results of comparative tests of EEs sensitized with various types of sensitisers (Tab. 6 and 7) show that greatest values of detonation rate, brisance and explosion heat were obtained for mixtures sensitized with magnesium hydride. This may be a result of i.a. that glass microspheres are inert additive.

Often used modifier of detonation and thermochemical parameters of the EEs is aluminium powder [18 – 20]. The paper [18] presents emulsion explosive matrix composed of ammonium nitrate (V), water and oil phase in % mass ratio 84/10/6 of density: 1.40 g/cm³. The matrix was sensitised with glass microspheres (DHMB) of 70 μm grains size and contained aluminium powder of average size of spherical particles equal to 6 μm, of the following content 0%, 10%, 20% and 30% (Tab. 9). Detonation rates measurements in 25/33 mm PVC pipes are presented in Figure 7.

Compositions and densities of tested EEs sensitized with DHMB [18]

No.	EES composition, %		Density g/cm³
	Matrix + 5% DHMB	Aluminium powder	
1	100	0	1.05
2	90	10	1.12
3	80	20	1.20
4	70	30	1.32
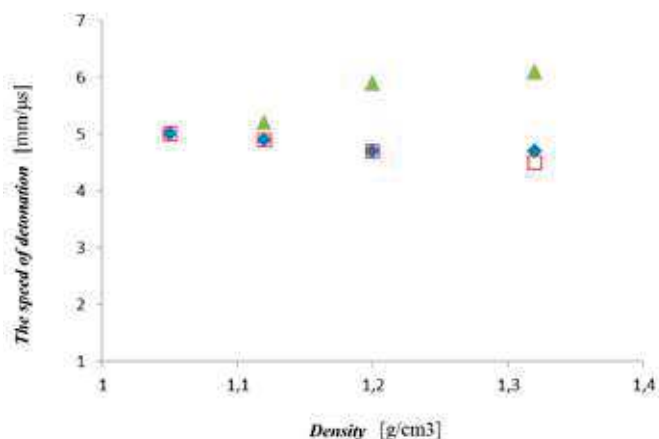
Fig. 7. Determined experimental and calculated detonation rate of EES: ♦ – experimental results, ▲ – 100% active aluminium powder, □ – 100% inert aluminium powder [18]

Data (Fig. 7) shows clearly that addition of aluminium powder under conditions of conducted experiments causes decrease in detonation rate of EES. Experiment results correspond to results of calculations obtained for assumption of 100% inertness of aluminium powder.

The paper [18] includes also determination of detonation pressure profiles for four compositions of various aluminium powder content. Firstly, measurements were conducted using manganin sensor placed on the end of charge between two Teflon layers of 0.4 mm thickness (on explosive side) and 25 mm. Then profile pressures were determined using Goransson's equation (3).

$$P_{ex}(t) = \frac{P_{tef}(t)}{2} \frac{(\rho U_s)_{tef} + (\rho D)_{ex}}{(\rho U_s)_{tef}} \qquad (3)$$
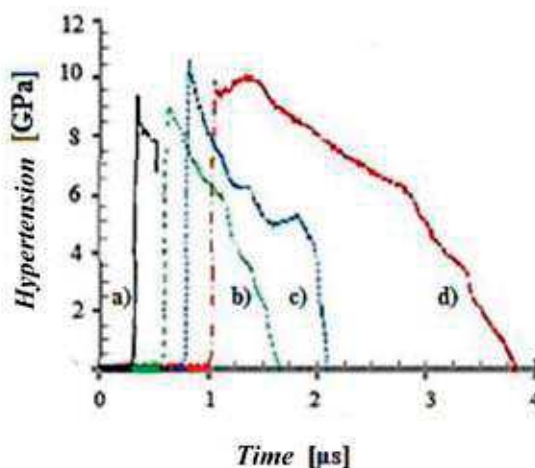
where:
D – detonation rate,
P_{tef} – pressure in Teflon partition,
ρo – emulsion explosive density,
U_s – shock wave velocity in Teflon.

Results of calculations performed based on experimental data are presented in Figure 8.

Fig. 8. Detonation pressure profiles for EEs of varying aluminium powder content: a) 0%, b) 10%, c) 20%, d) 30% [18]

Results (Fig. 8) show that maximum value of overpressure was obtained for 20% aluminium powder content despite the fact that previously detonation rate was found to decrease with increase of metallic additive content. It must be also noted that as the content of aluminium powder in explosive mixture increases, the overpressure peak wideness, which indicates the aluminium after-burns outside of chemical reaction zone of detonation wave.

The paper [22] studies 50/50 mixtures of EES matrix (composition: ammonium nitrate(V) – 72.0%, sodium nitrate(V) – 9.6, organic fuel and emulsifier – 7.4%, water – 11.0%) with trinitrotoluene (TNT) of varying degree of fineness. Detonation rate velocity measurements were conducted in thin-walled plastic pipes of 37 mm diameter. "Force of the explosion" was also determined by means of ballistic pendulum in comparison with blasting gelatine (BG) containing 90.75% of nitroesters. Experiment results are summarized in Table 10.

The next article [23] shows determination of detonatio rate for mixtures of EES matrix with composition B (component content: TNT – 46.0%; hexogen – 43.0%; organic additives – 11.0%) of grain size: 94% below 2 mm and 78% below 1 mm. Matrix composition was identical as in the previously referred paper [22]. Detonation rate measurement in polyethylene pipe of 37 mm diameter and "strength of explosion" determination as in paper [22] are summarized in Table 11 and Figure 9.

Table 10
Detonation parameters of EES containing trinitrotoluene [22]

TNT grain size μm	EES density g/cm³	Detonation rate m/s	Force of explosion in comparison with BG %
<200	1.45	5948	86.5
200–400	1.42	5887	89.0
400–800	1.39	5727	-
800–1600	1.43	5697	83.2
1600–4000	1.40	5452	85.5
>4000	1.40	5549	85.5

Table 11
Dependence of detonation rate (D) and "force of explosion" (FE) on content of composition B [23]

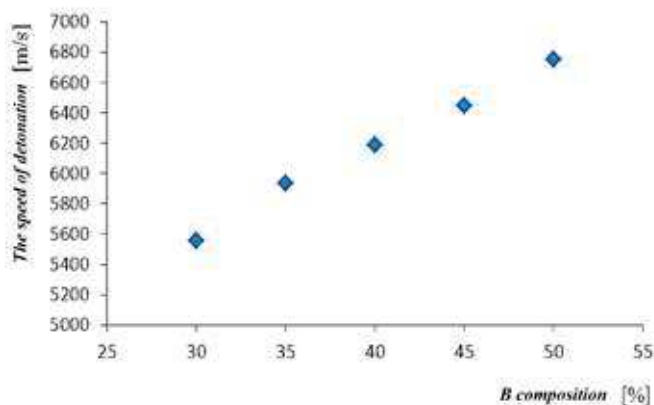| Composition, %		Measured and calculated parameters			
Matrix	Composition B	D, m/s	ρ0, kg/m³	ρ0D², GPa	FE, %
100	0	5160	1130	30.0	88.7
70	30	5559	1450	44.8	89.0
65	35	5932	1460	51.4	90.9
60	40	6189	1470	56.3	90.6
55	45	6449	1480	61.6	92.5
50	50	6749	1490	67.9	91.9

Fig. 9. Dependence of detonation rate of EES on content of composition B [23]

The paper [26] presents study of EE working capability performed using Held method and determination of intensity of air burst wave. EEs were sensitized with 0.8% addition of microballoons 461DET40d25 or 461DET80d25 and contained: 0%, 10%, 20% and 30% of sodium chloride. The matrix containing: oxidisers – 79.2%, organic phase – 6.0, water 14.8, complemented composition to 100%. The charges were of 400 g weight, of 180 mm length, 1.13 g/cm3 density and were placed in 46/50 mm hard PCV (tradename: winidur) pipes. The test system included two PCB pressure sensors at distances of 2.0 m and 2.5 m from explosive charge. The charges were activated using electrical fuse of ERG type. Measurement results of detonation rate and air burst wave intensity are presented in Table 12 and 13.

Table 12
Overpressure and overpressure pulse of burst wave generated as a result of EEs sensitized with microballoon 461DET40d25 and their detonation rate [26]

Composition	Explosive			
	MWE-MB-0	MWE-MB-10	MWE-MB-20	MWE-MB-30
Matrix	99.2	89.2	79.2	69.2
Microballoons 461DET40d25	0.8	0.8	0.8	0.8
Sodium chloride	-	10.0	20.0	30.0
Overpressure, kPa at distance:				
2.0 m	93.77	89.73	71.51	73.87
2.5 m	60.37	51.96	45.67	46.72
Overpressure pulse, Pa·s at distance:				
2.0 m	39.30	35.52	32.37	26.59
2.5 m	31.24	28.12	25.21	22.05
Density, g/cm³	1.04	1.05	1.08	1.08
Detonation rate, m/s	5090	4780	4480	4080

Table 13
Overpressure and overpressure pulse of burst wave generated as a result of EEs sensitized with microballoon 461DET80d25 and their detonation rate [26]

Composition, %	Explosive			
	MWE-MB-0	MWE-MB-10	MWE-MB-20	MWE-MB-30
Matrix	99.2	89.2	79.2	69.2
Microballoons 461DET80d25	0.8	0.8	0.8	0.8
Sodium chloride	-	10.0	20.0	30.0
Overpressure, kPa at distance:				
2.0 m	91.98	86.35	63.25	65.53
2.5 m	56.17	53.58	44.63	43.55
Overpressure pulse, Pa·s at distance:				
2.0 m	38.09	35.17	31.11	26.79
2.5 m	31.16	27.68	23.88	22.44
Density, g/cm³	0.97	0.95	1.04	1.05
Detonation rate, m/s	4770	4540	4270	3900

The results of the conducted experiments show that working capability and detonation rate of explosives depend on content of active ingredients that determined amount of energy released during high-energy reactions between oxidisers and combustible ingredients. Addition of sodium chloride as a cooling (inert) agent decreased explosion heat as this compound took no part in exothermic chemical reactions. At the same time sodium chloride particles in the chemical reaction zone, take the heat from explosion products obtaining thermal equilibrium. This caused significant drop in explosion product temperature and in pressure and, therefore, also decrease in measured detonation parameters.

Desensitization of EES under load of shock wave

High detonation performance of EEs is a result of their structure involving maximum homogenisation of oxidisers and combustible ingredients that provides their maximum conversion rate in chemical

reaction zone of detonation wave and gas filling additives that form "hot spots", where high-energy conversions are initiated, in a non-explosive matrix. Shock wave penetration into the EE that will not initiate detonation in the loaded material may cause its partial or complete desensitization due to emulsion inversion (crystallisation of oxidisers [29]) or deformation of hotspots. Y.F. Cheng et al. have studied effects of loading of explosion waves of varying intensity of EE charges sensitized with glass microspheres (content – 4%, grain size – 55 μm, bulk density – 0.25 g/cm^3) and H$_2$Mg (content – 2%, grain size – 3 μm, bulk density – 1.45 g/cm^3). EE samples of 30 g weight placed in container with water at various distances from hexogen detonator (hexogen/wax: 95/5, density – 1.45 g/cm^3) of 10 g weight (Fig. 10a). Then loaded samples were initiated with fuse and overpressure profile was determined by means of underwater tests; measurement system diagram is presented in Figure 10b, while measured overpressure profiles in Figure 11.
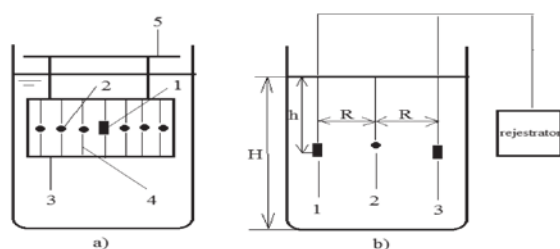

Fig. 10. Experimental systems, a) for loading EE with shock wave: 1 – hexogen detonator, 2 – tested EE, 3 – steel frame, 4 – steel wire, 5 – bracket. b) for overpressure measurement by means of underwater test: 1, 3 – sensors, 2 – tested EE charge [16]
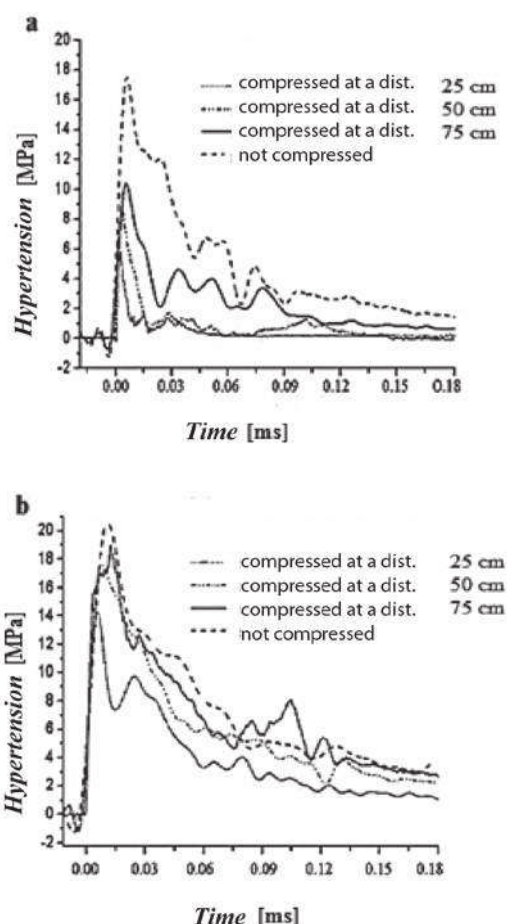

Fig. 11. Overpressure curves in time for EEs sensitized with a) glass microspheres, b) H$_2$Mg [16]

Based on the results obtained it may be concluded that maximum values of overpressure peaks for EEs sensitized with H$_2$Mg are much higher than for EEs sensitized with GHMB (Tab. 14).

Table 14

Average peaks of shock wave overpressure generated as a result of initiation of the EEs sensitized with glass microspheres and H$_2$Mg [16]

Distance of loading the EE charge, cm	Average peak of shock wave overpressure generated as a result of initiation of previously loaded charge, MPa	
	EE+glass microspheres	EE+H$_2$Mg
25	5.81	14.77
40	7.63	17.66
50	8.42	18.63
60	9.16	18.87
75	10.36	18.68

Based on maximum values of overpressure, the authors of paper [16] estimated desensitization degree (Sd) (Tab. 15) of loaded EEs using the formula (4):

$$S_d = (P_0 - P_1)/P_0 - P_d)$$ (4)

where:

P_0 – overpressure peak of not loaded EE,

P_1 – overpressure peak of loaded EE,

P_d – overpressure peak of fuse.

Table 15

Desensitization degree of two types of emulsion explosives vs distance of detonator [16]

Distance of loading the EE charge, cm	Desensitization coefficient, %	
	EE+glass microspheres	EE+H$_2$Mg
25	100	38.97
40	86.41	18.89
50	79.82	12.11
60	73.67	10.45
75	63.64	11.76

Data (Tab. 15) clearly shows that emulsion explosives sensitized with addition of magnesium hydride are much more resistant to desensitizing shock wave. Authors of paper [16] interpret the obtained results in the following manner: under effect of shock wave some glass microspheres crumbles and losses their sensitizing properties, while for magnesium hydride, hydrogen bubbles are flexible and after being squashed can return to original form. They also believe that only part of magnesium hydride reacts after its addition to the matrix. The remaining magnesium hydride can react as a result of shock wave (increase of temperature) and then so-called dynamic sensitization occurs.

Summary

Despite lack of significant evolution in the field of mining explosives, the recent years brought number of studies on the most often used blasting agents: saletrols (ANFOs) and emulsion explosives. There was particularly high number of papers on parameters of emulsion explosives. This is due to the fact that for example in comparison with ANFOs that at most are three-component mixtures of simple structures, the EEs contain many components that form very subtle metastable structure providing good detonation parameters. Multicomponent character of the EEs causes that their detonation parameters and detonation performance is affected by numerous factors, which identification is a main focus of conducted experimental studies that will allow to understand better detonation mechanism of the EEs.

science • technique

Litrature

1. Maranda A., Gołąbek B., Kasperski J.: *Materiały wybuchowe emulsyjne*, Wydawnictwa Naukowo-Techniczne, Warszawa 2008.
2. Information of State Mining Authority, Katowice, February 2014.
3. Maranda A.: *Przemysłowe materiały wybuchowe*. Wyd. Wojskowa Akademia Techniczna, Warszawa 2010.
4. Dobrilovič M., Bohenek V., Škrelec V.: *Influence of the initiation energy on the velocity of detonation of ANFO explosive*. Central European Journal of Energetic Materials 2013, **10**, 4, 555–568.
5. Dobrilovič M., Bohenek V., Žaganec S.: *Influence of explosive charge temperature on the velocity of detonation of ANFO explosives*. Central European Journal of Energetic Materials 2014, **11**, 2, 191–197.
6. Dobrilovič M., Bohenek V., Škrelec V.: *Velocity of detonation of low density ANFO mixture*. Proc. 16th Seminar on New Trends in Research of Energetic Materials, Pardubice, Czech Republic, April 10–12, 2013, **vol. II**, 543–554.
7. Žaganec S., Dobrilovič M., Bohenek V.: *Borehole velocity of detonation of ANFO and heavy ANFO explosives*. Proc.17th Seminar on New Trends in Research of Energetic Materials, Pardubice, Czech Republic, April 9–11, 2014, **vol. II**, 1080–1085.
8. Maranda A., Paszula J., Zawadzka-Małota I., Kuczyńska B., Witkowski W., Nikolczuk K., Wilk Z.: *Aluminum powder infuence on ANFO detonation parameters*. Proceedings of the 14th Seminar on New Trends in Research of Energetic Materials, Pardubice, Czech Republic, April 13–15, 2011, **vol. II**, 822–832.
9. Wang L., Fang J.: *Rheological properties and water-in-oil structure stability of emulsion matrixes*. Central European Journal of Energetic Materials 2013, **10**, 1, 87–102.
10. Wang L. Q., Wang N. F., Fang J.: *Rheology of typical emulsifiers and effects on stability of emulsion explosives*. Journal of Beijing Institute of Technology 2011, **20**, 3, 295 300.
11. Ligiong W., Jie F.: *Relationship between rheological properties and stability of emulsion matrix*. Proc.15th Seminar on New Trends in Research of Energetic Materials, Pardubice, Czech Republic, April 18–20, 2012, **vol. I**, 321–331.
12. Zhou H. S., Xie X. H., Xu K.: *Stability test of emulsion matrix in the emulsifier. Advanced Materials Research* 2015**,** 1082, 26–29.
13. Xu Z., Liu D., Hu Y., Ye Z., Wei Y.: *Influence of iron ion on thermal behavior of ammonium nitrate and emulsion explosives*. Central European Journal of Energetic Materials 2010, **7**, 1, 77–93.
14. Maranda A., Paszula J., Drobysz B.: *Badania parametrów detonacyjnych materiałów wybuchowych emulsyjnych o niskiej gęstości modyfikowanej mikrobalonami*. CHEMIK 2014, **68**, 1, 17–22.
15. Mendes R., Ribeiro J., Plaksin I.: *Differences between the detonation behavior of emulsion explosives sensitized with glass or with polymeric microballoons*. Journal of Physics: Conference Series 2014, **500**, 5, 520–530.
16. Cheng Y. F., Ma H. H., Shen Z. W.: *Detonation characteristics of emulsion explosives sensitized by H2Mg*, Combustion. Explosion and Shock Waves 2013, **49**, 5, 614–619.
17. Cheng Y. F., Ma H. H., Liu R., Shen Z. W.: *Pressure desensitization influential factors and mechanism of magnesium hydride sensitized emulsion explosives*. Propellants, Explosives, Pyrotechnics 2014, **39**, 2, 267–274.
18. Mendes R., Ribeiro J., Plaksin I., Campos J.: *Non ideal detonation of emulsion explosives mixed with metal particles*. AIP Conference Proceedings 2012, 1426, 267–270.
19. Wang L., Wang N., Zhang L.: *Study on key factors affecting energy output of emulsion explosives in underwater explosion*. Propellants, Explosives, Pyrotechnics 2012, **37**, 1, 83–92.
20. Hagfors M., Saavalainen J.: *Underwater explosions-particle size effect of Al powder to the energy content of emulsion explosives*. Proc. 36th Annual Conference on Explosives and Blasting Technique, Orlando, Florida, USA 7–10 February 2010, **vol. I**, 191–206.
21. Mendes R., Ribeiro J., Plaksin I., Compos J., Farinha R.: *Non monotonic detonation velocity and pressure behavior of emulsion explosive*. Proc.13th Seminar on New Trends in Research of Energetic Materials, Pardubice, Czech Republic, April 21–23, 2010, **vol. I**, 221–228.
22. Němec O., Jungová M., Zeman S.: *Fortification of W/O Emulsions by Demilitarized Explosives*. Central European Journal of Energetic Materials 2011, **8**, 3, 193–209.
23. Němec O., Jungová M., Zeman S.: *Modification of W/O emulsions by demilitarized Composition B*. Propellants, Explosives, Pyrotechnics 2013, **38**, 2, 142–146.
24. Němec O., Novotný M., Jungová M., Zeman S.: *Preliminary verification of fortification of W/O type emulsions with demilitarized explosives based on TNT*. Proc. 14th Seminar on New Trends in Research of Energetic Materials, Pardubice, Czech Republic, April 13–15, 2011, **vol. II**, 877–885.
25. Němec O., Jungová M., Pelikan V., Zeman S.: *Note one determination of relative explosive strength of fortified W/O emulsions by means of ballistic mortar*. Proc. 15th Seminar on New Trends in Research of Energetic Materials, Pardubice, Pardubice, Czech Republic, April 18–20, 2012, **vol. I**, 248–253.
26. Maranda A., Paszula J., Nikolczuk K., Wilk Z.: *Materiały wybuchowe emulsyjne zawierające chlorek sodu uczulane mikrobalonami*. Przemysł Chemiczny 2011, **90**, 6, 1254–1259.
27. Huang W. Y, Wu H. B., Yan S. L.: *Relationship research between crystallization quantity of emulsion explosive and de sensitization degree under dynamic pressure*. Biotechnology, Chemical and Materials Engineering 2012, **393**, 1389–1393.
28. Wang L., Wang N., Zhang L.: *Study on key factors affecting energy output of emulsion explosives in underwater explosion*. Propellants, Explosives, Pyrotechnics 2012, **37**, 1, 83–92.
29. Huang W., Wu H., Yan S.: *Relationship research between crystalization quantity of emulsion explosive and desentization degree under dynamic pressure*. Advanced Materials Research 2012, 393–395, 1389–1393.

Andrzej MARANDA – Professor (Sc.D., Eng) is a graduate of the Faculty of Chemistry, Warsaw University of Technology (1971). Currently, he works for the Military University of Technology and the Institute of Industrial Organic Chemistry. Research interests: chemistry, technology and the use of explosives, protection of the environment. He is the author of 5 monographs, 20 patents, over 500 articles, papers and posters at national and international conferences.

e-mail: amaranda@wat.edu.pl, phone: +48 22 683 75 41

Ramona SITKIEWICZ-WOŁODKO - M.Sc., (Eng.), graduated from the Faculty of Advanced Technologies and Chemistry, Military University of Technology major in explosives and pyrotechnics (2012). Currently she enrolled in Ph.D. program at her alma mater. She is a co-author of two articles.