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Review

A Literature Review of the Influence of Water on the Properties of Mining Explosives

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Abstract: The review presents the characteristics of the properties of explosive mixtures containing water as one of the basic components. The analytical work was conducted on AN/water binary mixtures, ANFO, watergel and emulsion explosives. Work conducted on a hydrogen peroxide-based watergel explosive was also included. The most frequently described parameters were the explosive transformation capacity, detonation velocity, and content of toxic components in the explosion products.

Keywords: water, ammonium(V) nitrate, ANFO, slurry explosives, emulsion explosives, detonation parameters

1 Introduction

Explosives used in the mining industry are usually mixtures, the components of which are characterized by different physical and chemical properties, e.g. density, viscosity, water resistance or high-energy parameters [1]. 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 components in explosives is water. Depending on the type of explosive, water could act either as an undesirable or a required component. The component causing deterioration of utility properties is water in the case of non-water-resistant explosives, which include ammonites and ANFO, for example, water is an undesirable material in AN/ANFO, where AN denotes ammonium nitrate(V) (NH_4NO_3) and FO denotes fuel oil, as these material degrade during storage. Furthermore, water present in a blasthole dissolves ANFO, causing misfires or nitrogen oxides (NO_x) fumes after blasting. On the other hand, in the case of suspension and emulsion explosives, water plays the role of a texturing component, enabling the formation of an a blasting agent which is safe to transport on public roads, pumpable, and with better water proof properties than ANFO, and therefore the possibility of use in water-logged holes. Water, as a chemically inert component, also affects the detonation parameters of explosive mixtures, which are presented in this paper.

2 Binary Mixtures AN/Water

Aqueous concentrated solutions of AN are an intermediate material used in the production of emulsion explosives. In order to determine their potential explosive properties, to determine their detonation potential regarding safety in the production process, detonation capability and detonation velocity were investigated [2]. The experiments were conducted in insulated steel pipes with an inner diameter of 6 inches. Inside the pipe, a heating element enabled the AN solutions to be heated in a range of 127-152 °C. The density of the solutions was reduced to 0.8, 1.0, and 1.2 g/cm^3 , by aeration. The pH of the solutions was varied and adjusted by the addition of nitric acid (HNO_3). 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 had occurred. 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.

Table 1. Results of detonation velocity measurements of AN solutions [2]

Concentration of aqueous solution of AN [%]	pH of the solution	Temperature [°C]	Detonation velocity [m/s]	Fraction detonation
83.0	2.5	126.9	2180	0
84.0	~8	144.4	2280	0.25
88.5	2.0	151.9	2280	0.25
88.5	~8	150.4	2470	0.40
95.0	~2.5	152.4	2040	1.00

The results show that even at relatively low concentrations (83.0%) of aqueous solution, air bubbles cause sensitization. The authors do not provide the size of the gaseous inclusions but believe that these are larger than typical sensitizers of emulsion explosives such as glass microspheres or plastic microballoons. 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, as yet, has no theoretical explanation [2].

3 Water Content Due to Mining Explosive Properties

3.1 ANFO

In 1955 the Cleveland Cliff Company conducted the first industrial blasting using ANFO (a mixture of 94.5/5.5 of AN and fuel oil [1, 3]). Since then, various studies of the performance and detonation parameters have been conducted. Experiments performed in recent years have involved, among others, the effects of different types of additives on the detonation parameters [4-7], density [8], temperature [9], and booster mass [10] on the detonation velocity. Studies of physico-chemical properties of potential flammable liquid components [11, 12] and the morphology of their basic component, AN [13, 14], have also been carried out.

The primary disadvantage of ANFO explosives is their lack of water resistance. Yancik, [15], describes the decrease in detonation velocity of ANFO explosives after the addition of water. He showed that the addition of 7-8% water causes a 12-14% decrease in the detonation velocity, and the addition of 9% water reduces the detonation velocity by 38-40%. However, totally different results were obtained by Araos and Onederra [7]. They studied the detonation velocity of nitres in 105 mm diameter charges placed in plastic tubes. These mixtures, containing 0%, 3%, 6%, and 9% of water, had very similar to detonation velocities, in a range of 3130-3210 m/s. In the tests conducted by Yancik, due

to its porosity, the type of AN was much worse than the samples currently used in experiments [7]. Then, Baron and Kantor [16] presented the results of ANFO detonation velocity tests as a function of water content (Figure 1). The experiments were conducted in 38 mm diameter blast holes. Figure 1 also presents the results of detonation velocity tests carried out in 75 mm diameter pipes [17].

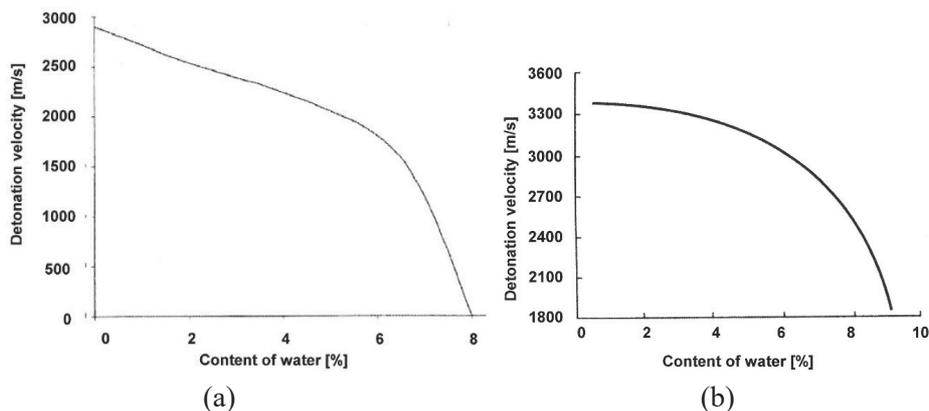


Figure 1. Dependence of ANFO detonation velocity on water content according to [16] (a) and [17] (b)

The low influence of water on the detonation velocity of an AN-based explosive at its low concentration was confirmed by data compiled by Zygmunt *et al* [18]. Detonation velocities of AN-based explosives containing water in the range of 0.4-6.6%, were found to be in the range of 2490-2630 m/s.

Furthermore, Biessikirski *et al.* [19] conducted gases analysis studies on post blasting from ANFO at different water contents. ANFO samples (AN/FO 94/6) weighing 600 g, containing porous AN with a bulk density of 0.705 g/cm³, were initiated in a steel mortar with a hexogen booster weighing 14 g. The results are presented in Table 2.

Table 2. Volume of toxic shot gases in ANFO explosion products containing different amounts of water [19]

Water content [%]	Volume of gunshot gases [dm ³ /kg]				
	CO	NO	NO ₂	NO _x ^{*)}	Sum
0	18.80	8.54	0.58	7.12	25.92
1.5	17.38	0.41	0.06	0.47	17.85
3.0	17.51	0.58	0.30	0.88	18.39
4.5	9.35	2.37	0.14	2.51	11.86
6.0	7.35	7.50	0.72	8.21	15.56
7.5	7.35	6.47	0.83	7.30	14.65

*) NO_x is the total sum of the NO and NO₂ by volume

The data presented in Table 2 show that with the increase in water content, the volume of carbon monoxide decreases, the minimum volume of nitrogen oxide(II) occurring at a water content of 1.5%, with the total volume of toxic explosion products being the lowest at a water concentration of 4.5%. Of course, the decrease in the volume of carbon monoxide with an increase in water concentration in the explosive mixture is determined by the increasing content of ANFO. However, the changes in the volume of nitrogen oxides are very difficult to interpret: this would have been possible if Biessikirski *et al* [19] had measured the detonation velocities of the tested explosive mixtures.

3.2 Slurry explosives (SEs)

The lack of water resistance of ANFO explosives which prevented them from being used in waterlogged holes, and the approaching expiration of wartime ammunition stocks, have proved to be stimuli for the development of new mining explosives. One very important research result was the development of the first versions of SE by Cook and Farnam [20]. Cook [21] also proposed the division of SEs into two types: *Slurry Explosives* (SEs), sensitized by military explosives, and *Slurry Blasting Agent* (SBA).

The basic components of SEs are the explosives-water systems described above and AN. The continuous phase is a saturated solution of AN, with the dispersed phase comprising a solid explosive and the undissolved part of the oxidizers. Sedimentation of the solids is hindered by the addition of thickening agents to the liquid phase. This additive also causes high water resistance in slurry explosives.

The most popular component used was TNT (SE-TNT). The detonation parameters of SE-TNT are mainly dependent on the TNT content, as well as water concentration. Vetluzhskickh *et al.* [22] studied the detonation velocities

of SE-TNT charges with different water content, placed in asbestos-cement pipes with an inner diameter of 100 mm and initiated with a 400 g TNT booster. The detonation velocities were 5520, 5210, and 5120 m/s at water contents of 10%, 15% and 20%, respectively.

Different results of the effect of water on the detonation velocity of explosives sensitized with hexolite (SE-HT), were obtained by Yoffe and Menshikov [23]. The hexolite pellets investigated contained 80% TNT and had an average particle size of 3-5 mm, with an additional variable connected with the average particle size of the oxidizers (ammonium and sodium nitrate). The results of the detonation velocity measurements are illustrated in Figure 2. Yoffe and Menshikov also determined the effect of water content on the critical diameter and detonation capacity of the SE-HTs, characterized above. The results of the experiments are summarized in Figure 3.

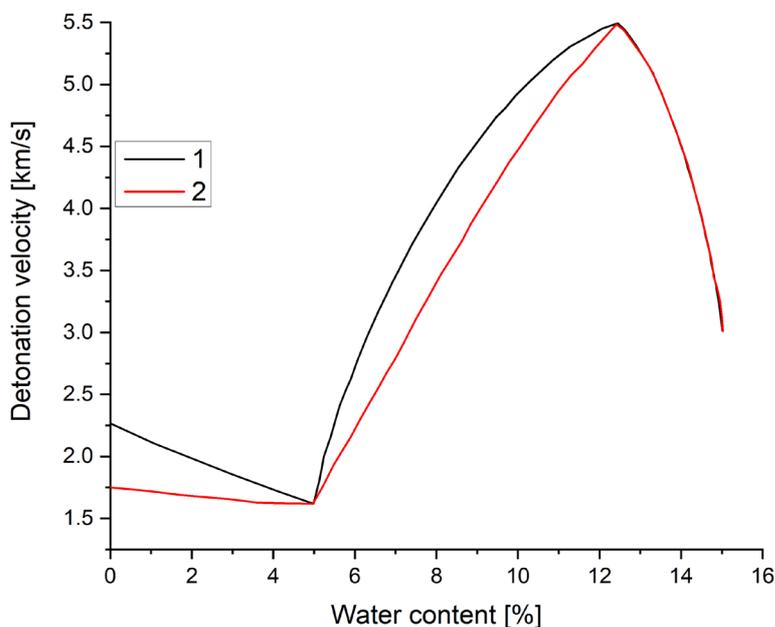


Figure 2. Dependence of detonation velocity of SE-HT on water content and oxidant fineness: 1 – <0.56 mm and 2 – 1-2 mm [23]

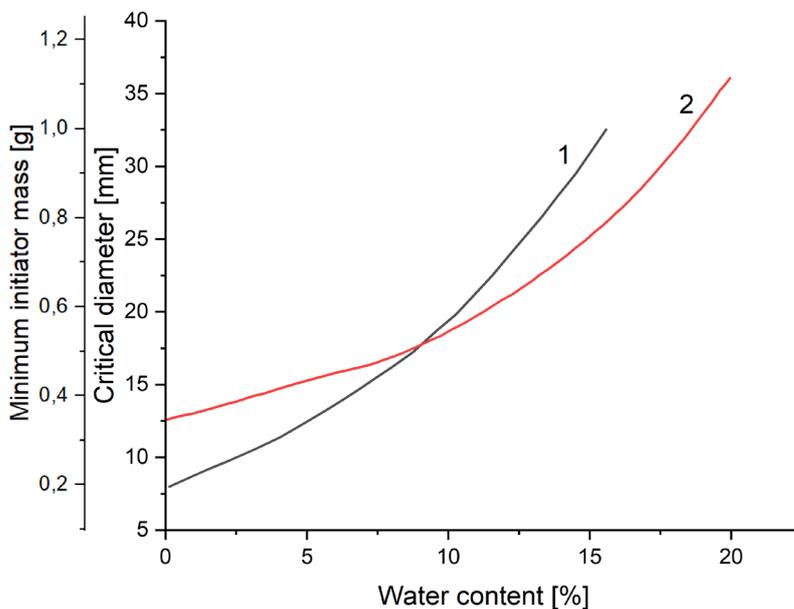


Figure 3. Effect of water content on the: 1 – critical diameter of SE-HT and 2 – minimum initiator mass [23]

The Yoffe and Menshikov results showed that SE-HTs reached their maximum detonation velocity at a water content of 12.5% and that their detonation capability decreased with increasing water content. The most popular slurry explosives, classified by Cook [21] as Slurry Blasting Agent, were explosives sensitized with high-grade aluminum dust – usually flake (SE-Al). In the 1970s-90s, their detonation parameters were described in a number of publications issued by the Military University of Technology [24-29]. Among other factors, the influence of water on the critical diameter and detonation velocity was studied. In [24], the critical diameter of SE-Al as a function of density, was determined at two water content levels (Figure 4). [18] shows the results of the water content effect on the critical diameter of SE-Al containing different amounts of flake aluminum dust. The results of the measurements are illustrated in Figure 5.

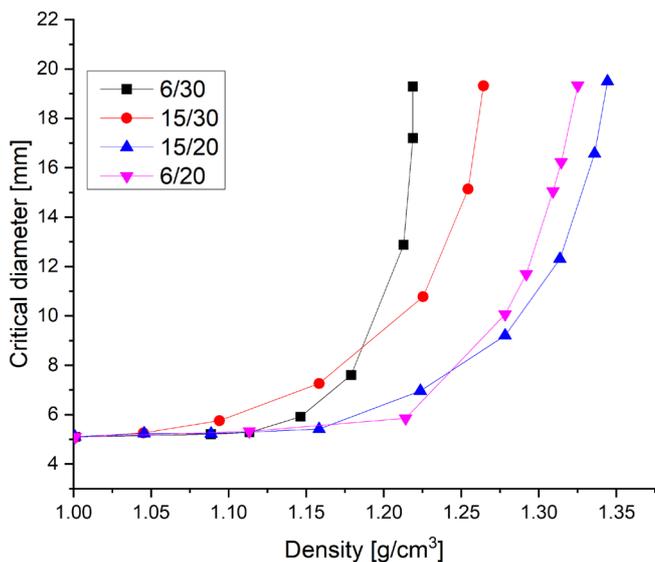


Figure 4. Dependence of SE-Al critical diameter on density at different aluminum dust/water contents [22]

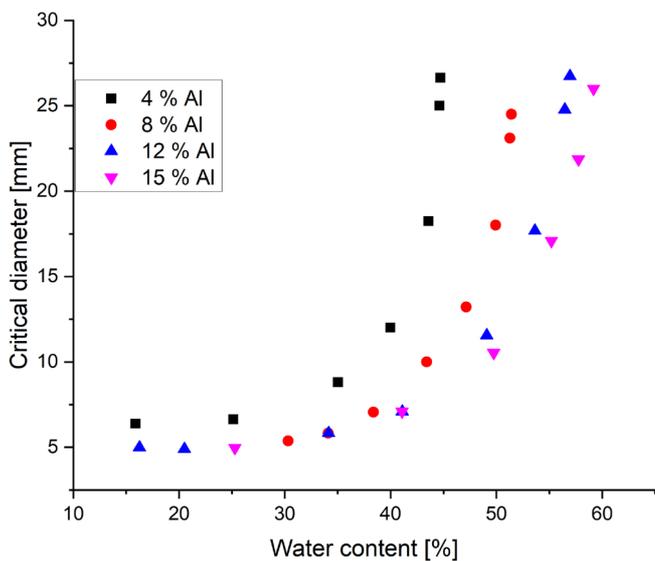


Figure 5. Effect of water content on the critical diameter of SE-Al [18]

In other work [27], the effect of water on the detonation velocity of mixtures of aluminum dust (4%) and AN was determined. The procedures in the study

were continued until a suspended explosive structure was obtained ($> \sim 12\%$ water). The results of the experiments are illustrated in Figure 6.

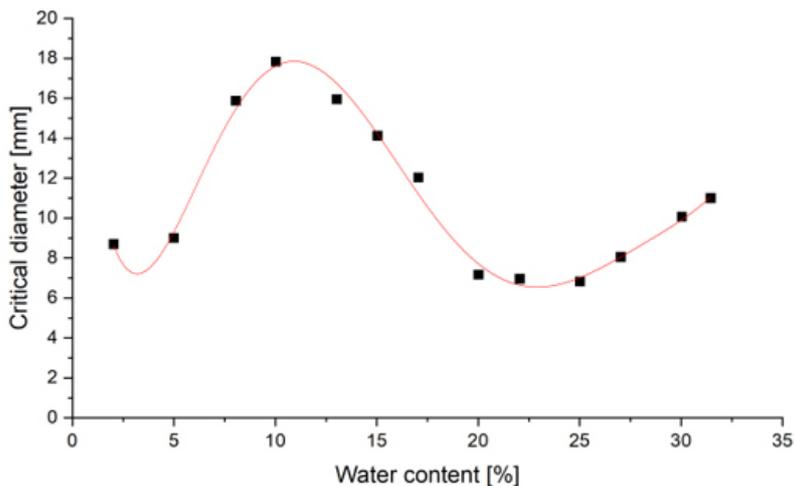


Figure 6. Dependence of critical diameter of SE-Al on water content [28]

The dependence of the detonation velocity of SE-Al on water content has also been measured [19, 28]. In studies [25, 28] the mixtures examined contained 6% of metallic additive with measurements being conducted in paper tubes with a diameter of 18 mm. The detonation velocity was determined as a function of the degree of aeration (Figure 7(a)) and density (Figure 7(b)) of the explosive system.

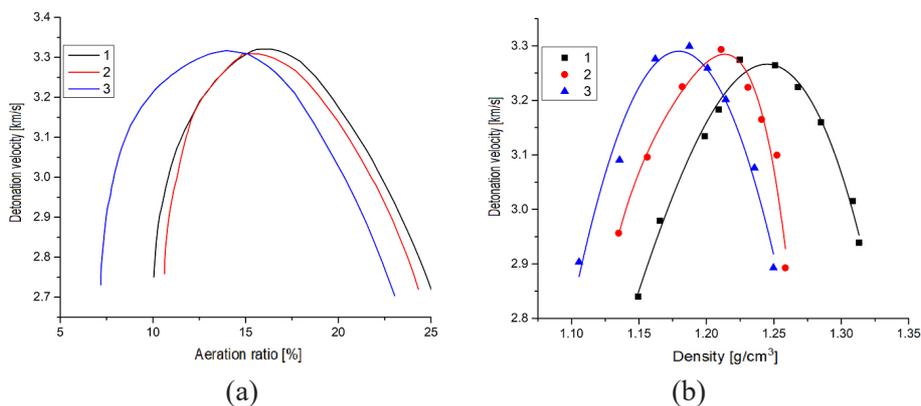


Figure 7. Dependence of SE-Al detonation velocity on the degree of aeration (a) and density (b), for water content of: 1 – 20%, 2 – 25% and 3 – 30% [25, 28]

Zygmunt *et al.* [18] present the results of measurements of the effect of water on the detonation parameters of SE-Al performed by an electromagnetic method. The experiments were conducted in 36/40 mm vinyl tubes. The results of the experiments are summarized in Table 3.

Table 3. Detonation parameters of SE-Al as a function of water content [18]

Water content [%]	25	35	44	50	53
Density [g/cm ³]	1.17	1.15	1.08	1.06	1.04
Detonation velocity [m/s]	4500	4450	4020	3600	2710
Mass velocity [km/s]	1040	1060	920	720	540
Pressure at C-J [GPa]	5.5	5.4	4.0	2.7	1.5
Reaction time [μ s]	0.68	0.64	0.75	1.03	1.24
Reaction zone width [mm]	2.2	2.0	2.2	2.7	2.5
Polytrope exponent	3.3	3.2	3.4	4.0	4.0

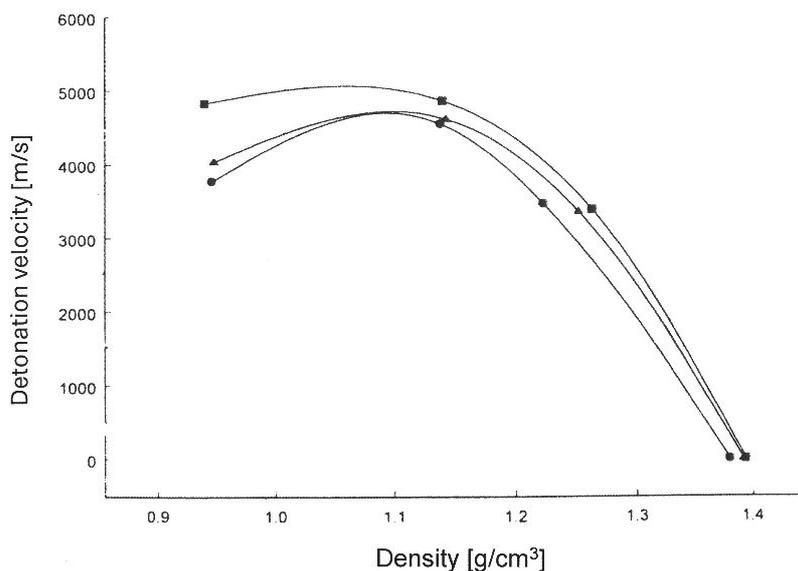
From the detonation velocity measurements presented above, it is clear that an increase in the water content of SE-Al, causes a decrease in detonation parameters. Water is an energetic ballast but plays an important textural role, providing an appropriate structure, giving aluminium slurry explosives low sensitivity to mechanical stimuli and high water resistance. These two factors make it possible to mechanize SE-Al loading into blastholes, which can be dry or waterlogged.

3.3 Emulsion explosives (EMs)

EMs were patented in 1969 by Bluhm [30]. Although more than fifty years have elapsed, EMs are considered the most modern mining blasting agents. The emulsion explosives' matrix is a water-in-oil emulsion with no detonation capability. It is sensitized by the introduction of gas bubbles by chemical or physical means. Work has been conducted mainly on the effects of stability [31, 32] and type of sensitizers [33-35] on their basic properties. Detailed studies of the effect of water on the properties of EMs were carried out by Allum *et al.* [36]. In the first cycle of studies, they determined the effect of water content (12-35%) and glass microsphere (1.0%, 2.5%, and 5%) on the density of EMs (Table 4). They then conducted tests on the effect of density on detonation velocity (Figure 8), with detonability and brittleness being determined by the plate dent test.

Table 4. Density versus water and glass microspheres content [36]

Sample	1	2	3	4	5	6
Component [%]						
– Glass microspheres	1.0	1.0	1.0	1.0	1.0	1.0
– Water	12	15	20	25	30	35
Density [g/cm ³]	1.26	1.25	1.22	1.19	1.15	1.111
Sample	7	8	9	10	11	12
Component [%]						
– Glass microspheres	2.5	2.5	2.5	2.5	2.5	2.5
– Water	12	15	20	25	30	35
Density [g/cm ³]	1.14	1.14	1.14	1.11	1.07	1.05
Sample	13	14	15	16	17	18
Component [%]						
– Glass microspheres	5.0	5.0	5.0	5.0	5.0	5.0
– Water	12	15	20	25	30	35
Density [g/cm ³]	0.96	0.95	0.95	0.92	0.89	0.86

**Figure 8.** Variations in the velocity of detonations with density, water: ■ – 12%, ▲ – 15% and ● – 20% [36]

It was found that the highest detonation velocity and detonation ability were observed for the EM containing 12% water and 2.5% glass microspheres at a density of 1.14 g/cm³. Based on the relationship between detonation velocity and density obtained, Allum *et al.* [36], using the classification proposed by Price [37], classified the EM to the second group of high-explosives (non-ideal EM).

The effect of water on the critical diameter and detonation velocity of EMs was then determined by Maranda *et al.* [38]. They studied the critical diameter as a function of the amount of water for mixtures containing 4.1% oil and 15% glass microspheres (Figure 9(a)). The detonation velocity of EMs as a function of water content was measured in charges of 9.1% microsphere content (Figure 9(b)).

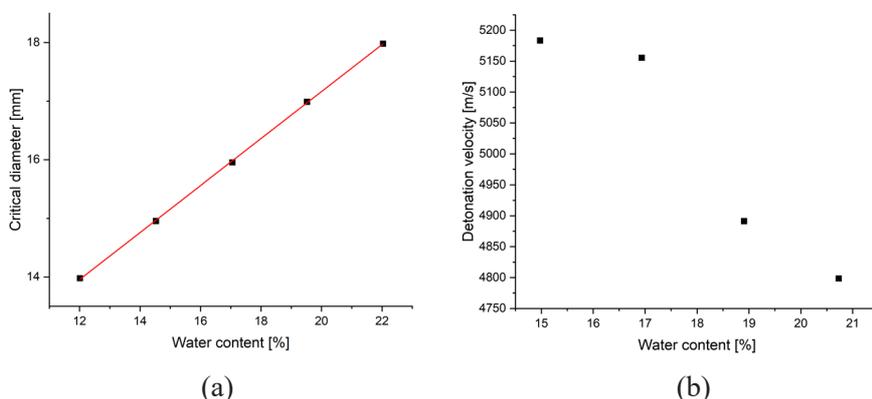


Figure 9. Effect of water content on critical diameter (a) and detonation velocity (b) of EMs [38]

The results of the emulsion explosives' critical diameter measurements presented above show that there is an increase in the measured parameter. The addition of glass micro balloons (GMB) causes a dilution of the explosive. Moreover, the GMB consumes heat from the detonation and therefore lowers the high-energy parameters.

Another parameter of emulsion explosives which has been measured is their minimum combustion pressure. Turcotte *et al.* [39] studied EMs with content ranging from 11.7% to 24.8%. They observed that with increasing water content the minimum combustion pressure increased.

3.4 Hydrogen peroxide explosives (HE-HP)

The first publication on the explosive properties of mixtures containing hydrogen peroxide (HE, H₂O₂) was published in 1927 [40]. Mixtures of H₂O₂ with alcohols (ethanol, methanol, glycerol) were studied in Germany between 1938 and 1944.

A number of tests were performed using varying concentrations of H_2O_2 solution from 61% to 100%. A significant number of measurements were made for charges in an aluminum tube with an inner diameter of 21 mm, initiated with a primer reinforced with 10 g of pentaerythritol tetranitrate (pentrite). The detonation velocity decreased linearly from a value of 6800 m/s for HP100 to about 6000 m/s for HP72.3. At a concentration of HP61 the samples did not detonate [36].

After the end of World War II, research was continued by Shanley and Greenspan [41]. This research resulted in a patent obtained in 1948 [42]. Mixtures based on H_2O_2 , water and glycerin were prepared in a single-phase system which was relatively stable and unreactive at room temperature. The resulting explosives were not very sensitive to mechanical stimuli but detonated when initiated with a standard primer. A very important result of the study was the development of a triangular diagram (Figure 10) of the detonation range of explosive mixtures containing H_2O_2 , glycerin, and water. The double hatched area covers the zone in which the H_2O_2 /glycerin/water system, detonates.

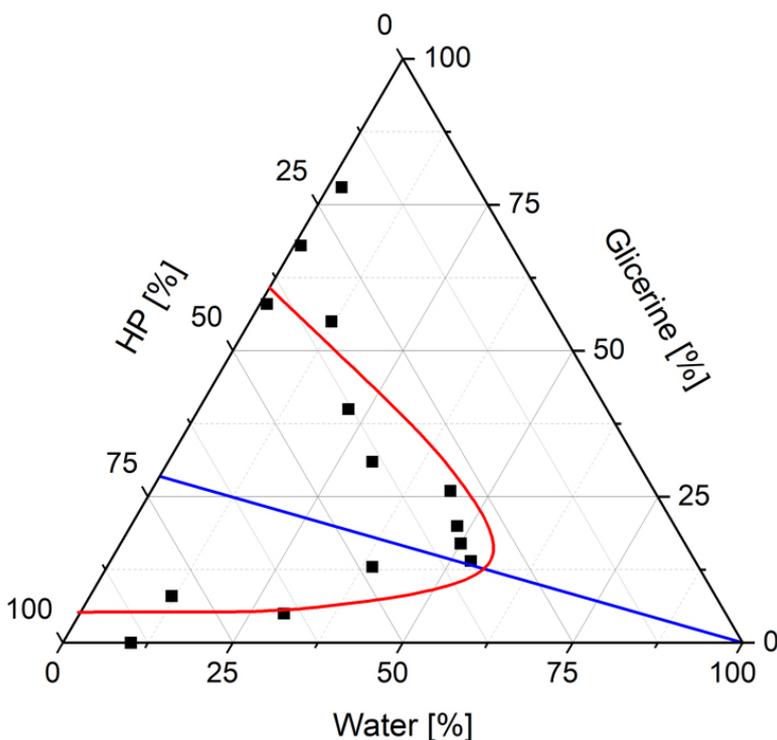


Figure 10. Triangular detonation range diagram of H_2O_2 /glycerol/water system [42]

Further work on explosive mixtures of aqueous solutions of H_2O_2 and glycerin was carried out in the 1960s by Baker and Groves [43]. They proposed mixtures with explosive properties containing H_2O_2 , mainly in a concentration range of 75% to 90%, with numerous additives, which were fillers with the nature of absorbents. The additives were mostly of natural origin. Another group of additives mentioned in the patent were phenol-formaldehyde and urea-formaldehyde resin, powdered metals (aluminum, tin), and gelling agents. The mixtures proposed by the patent authors detonated using primer No. 6 [44].

The topic was then pursued at various research centers. Amongst other outcomes, the work resulted in a patent by Bouillet *et al.* [44] in which the explosive properties of cross-linked mixtures of monomers with an 85% aqueous solution of H_2O_2 were presented. The highest detonation velocity (above 7000 m/s) was obtained by the authors of a patent for a sucrose/dipicolinic acid/acrylic acid/85% aqueous solution of H_2O_2 195/0.39/130/975 composition with a density of 1.38 g/cm³. Detonation velocity measurements were made in 33/37 mm polyvinyl chloride (PVC) tubes.

Schreck *et al.* [45] tested mixtures of aqueous H_2O_2 solutions with various alcohols for their safe transport. As fuel, they used 2-propanol (P-ol) and 2-methyl-2-butanol (MB-ol). They determined the ability of the ternary mixtures to undergo high-energy transformations and conducted the latter measurement in 50/60 mm steel pipes. They succeeded in demonstrating that the ability to detonate, under the conditions of their experiments, has $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{P-ol}$ 31/62/7 and $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{MB-ol}$ 40/52/8 mixtures.

Experiments performed in Australia included determining the effect of H_2O_2 concentration (and thus indirectly water content) on the detonation parameters of HE-HP [46-48]. In their work [48], Araos and Onederra tested HE-HP with a small negative oxygen balance containing 41.5%, 51.6% and 56.55% water. In their first phase of experiments, they showed that HE-HPs sensitized with chemical (GS) and GMB containing 56.55% water failed to detonate in 102/104 mm diameter PVC pipes, with a density range of 0.55-0.90 g/cm³. As a result, they conducted further studies for the other two water contents. They carried out thermodynamic calculations of detonation pressure and velocity as a function of density and obtained small differences in the determined parameters for HE-HPs containing 51.6% and 56.55% water and different density (Figure 11).

Araos and Onederra then experimentally determined the detonation velocities of HE-HP sensitized with GMB containing 41.5% and 51.6% water. They conducted the measurements in 102/104 mm PVC pipes. Charges were initiated with 50 g pentolite boosters. From the results of the measurements, summarized in Figure 12, it can be seen that, unlike in the case of thermochemical

calculations, the detonation velocity does not increase over the entire range of density, but up to a certain value, which for the conditions of the experiments can be considered optimal. Also, there is a very large difference (~ 1200 m/s) between the detonation velocities of HE-HP containing 41.5% and 50.6% water. It should be noted that the maximum detonation velocity of HE-HP containing 41.5% is about 5500 m/s, which places the HE in question at the level of EMs.

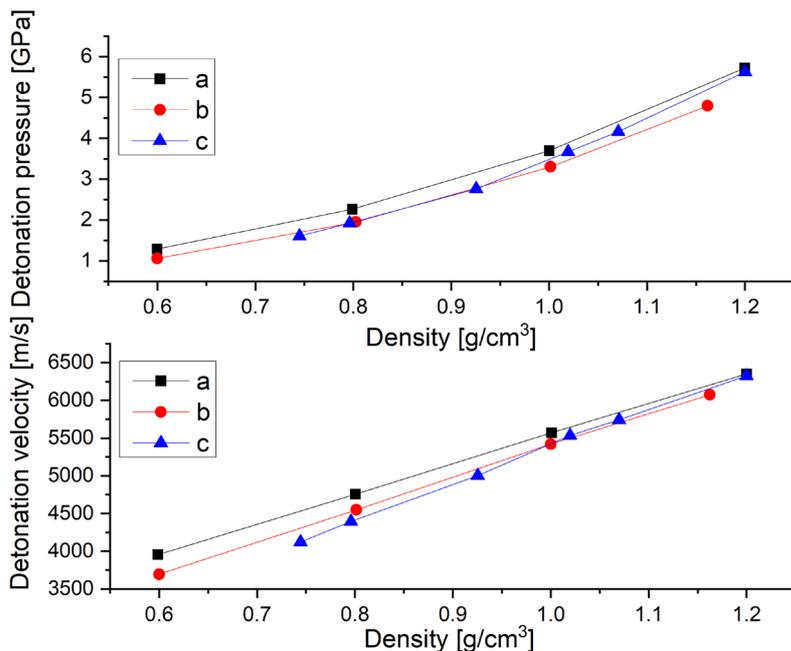


Figure 11. Thermodynamic calculations of HP/fuel-based mixtures: a – water 41.5% + GS, b – water 51.6% + GS and c – water 51.6% + GMB [48]

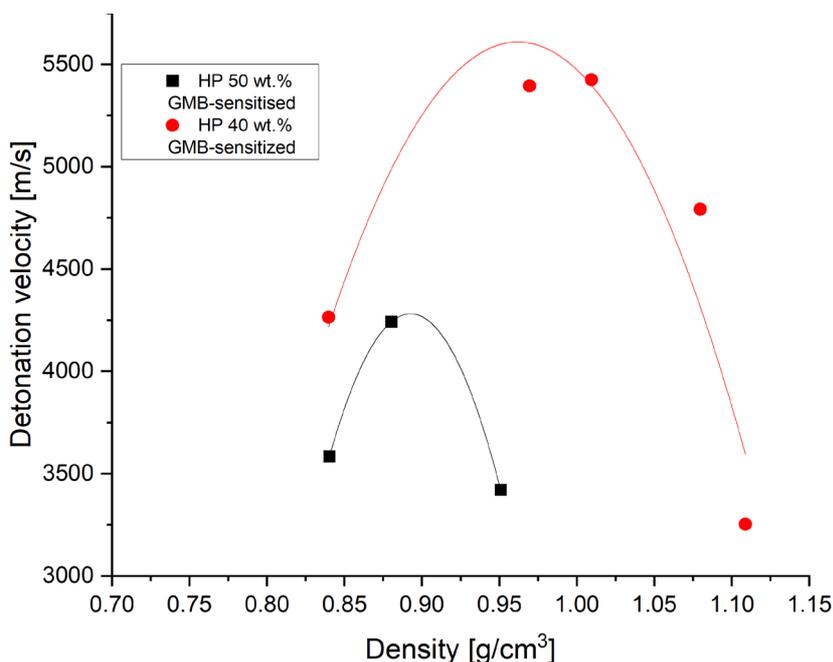


Figure 12. Density vs detonation velocity relation at different water contents: a – water 41.5% + GMB and b – water 51.6% + GMB [48]

Based on the data obtained in paper [48], it can be concluded that the limiting water content of HE-HP is at least about 50%. This value is much higher than in the case of ANFO – less than 9% [15], or EMs – 35% [22]. This is due to the structure of HE-HPs, which are an ideal mixture of an oxidizer (H_2O_2) and a combustible component (such as glycerin). A reflection of the ideal structure of HE-HPs (from the point of view of the detonation process) is their critical diameter. In [48], its minimum value of less than 8 mm is reported.

4 Summary

- ◆ This literature review shows that water plays an important role in explosive mixtures. It affects their basic parameters, detonation capacity, detonation velocity, and also application. In most cases, it is chemically inert. However, its main task, especially in ammonium-salt explosives, is to form a suitable texture thereby ensuring partial (slurry explosives) or complete (emulsion explosives) dissolution of ammonium nitrate(V).

- ◆ As a result of this physical process, ammonium nitrate(V) is better suited for high-energy transformations, which is reflected in the low critical diameters and high detonation velocities of slurry and emulsion explosives compared to ANFO. For these two types of explosives, the use of water makes it possible to provide very high water resistance.

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