

Article

Composition of Fumes and Its Influence on the General Toxicity and Applicability of Mining Explosives

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Abstract: The admissible concentrations of toxic fumes, which appear after blasting works in open pits and underground mine excavations, are presented in this paper. Fumes were examined according to the national standard, which was designed according to European regulations. Fumes that are taken under consideration according to the European standard are carbon monoxide (CO) and nitrate oxides (NO_x). The afterburning effect was not included. Analysis showed inconclusive results of possible explosive applicability in countries that are applying the general toxicity index (toxicity coefficient may vary between countries from 5 to 10) instead of the recommended European regulation. Based on the obtained results, it was concluded that the most environmentally friendly explosives are emulsion explosives. Moreover, the ammonium nitrate prill diameter has not significantly affected the fumes' concentration; however, it significantly influences the velocity of detonation.

Keywords: explosives; fumes; general toxicity; mining



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1. Introduction

Blasting is one of the most commonly used mining techniques due to its low cost and a large volume of excavated rock mass in a short period of time. The most commonly used explosives in terms of mining (both underground and open-pit) are ANFO, emulsion explosives, and dynamites. According to (Standard and Poor's) S&P Global analysis, the largest consumers of explosives in industrial applications are China, the United States, the Commonwealth of Independent States, and Central and South America. Moreover, in spite of the mining industry, a significant volume of explosives is applied in civil works (construction industry) [1]. In terms of mining, coal mining is, according to S&P Global, the largest consuming sector for industrial explosives. It is responsible for ca. 40% of total explosives consumption. However, it was observed that with the energy shift towards green technology, and concerning the Paris Agreement which aims at the reduction of carbon dioxide, the coal mining output started to decrease which resulted in a smaller consumption of explosives [1]. In addition to coal mining, ore mining is responsible for ca. 33% of the world's explosive consumption. According to S&P Global analysis, this sector of the mining industry is projected to increase during the 2019–24 forecast period [1]. Stone quarrying for the construction and production of cement is responsible for 16% of the world's explosive consumption. Biegańska and Barański indicated that in 2020 in the Polish market, the consumption of ANFO and emulsion in open-pit mining was, respectively, ca. 7.02 million kg and ca. 17.88 million kg [2].

Oluwoye et al. estimated that the total NO_x emission rate in 2017 from AN-based explosives was ca 0.05 Tg (5×10^4 t) N per year [3]. They concluded that this is a minor share in comparison to the total global annual anthropogenic NO_x emissions which was evaluated as 41.3×10^6 t N per year [3]. However, Oluwoye et al. have indicated that despite this fact, blasting works emit a large localized plume of fumes of a high NO_x concentration (close to ca. 500 ppm) which exceeds up to 3000 times the permissible levels [3].

In terms of explosives, detonation is a type of chemical reaction, which occurs rapidly and results in a considerable volume of fumes (it is expected that around 1000 dm³ of fumes may appear from 1 kg of explosive in the assumption of optimal charge diameter). When the solid explosive is shocked, its temperature, pressure, and density rise sharply; consequently, a chemical reaction is triggered and a detonation wave is produced [4]. As a result of a chemical reaction, a large volume of high-pressure gases is obtained. The volume of fumes is proportional to the attained pressure. In addition, the composition of fumes is determined by the detonation heat. The heat directly affects the temperature resulting from product decomposition. In other words, the detonation process has the highest velocity, is strong enough to crush rocks, and provides the least amount of toxic substances [5]. On the other hand, some properties such as toxicity and melting point are also needed in the case of developing a new type of energetic material [6].

Since the 1960s, a strong emphasis has been put on the health and safety conditions of workers. Studies on the impact of toxic fumes on the human body have been carried out. Based on the findings, it has been determined that long-term exposure to a small concentration of nitrogen oxides (NO_x) and carbon monoxide (CO) can lead to respiratory problems. A higher concentration of toxic fumes can cause death. Obtained results by researchers in Poland, in the 1980s, contributed to the design of general standards (PN-C-86067) for maximum concentrations of toxic fumes in underground mining [7,8]. Access to the European Union resulted in the need to adjust the applicable national regulation to the European Union directive.

Evaluation of the emission of toxic fumes, which appear after the detonation process, is widely discussed in papers across the world [9–12]. To ensure the safety of workers and the environment, several analytical methods have been developed both in risk assessment [13] as well as in the evaluation of oxide's harmful potential in underground mines [14,15] and open-pit mining [16].

The evaluation of the volume of toxic fumes is generally provided in papers that are subjected to the blasting properties of the explosives, or packaging. Based on the volume of the CO and NO_x, Biessikirski et al. investigated fumes in the case of the addition of silicon dioxide, microstructure charcoal, various assortments of ammonium nitrate(V), or the application of different types of fuel oils [17–19]. Oluwoye et al. focused on the next type of explosive mixtures which are obtained by the application of new types of fuels or additives [3], Araos and Onderra evaluated fumes in the new type of hydrogen peroxide-based explosives [20]. Kuterasiński et al. researched the potential addition of zeolite Y type to the ANFO. One of his evaluated factors was fumes derived from the detonation of non-ideal explosives [21]. Bhattacharyya investigated the influence of packaging on the NO₂ and CO of semi-gel nitroglycerine-based explosives. They concluded that a bigger prill size of ammonium nitrate(V) results in a higher volume of fumes [22]. Torno and Toraño as well as Tiile made research based on the field detonation in the underground mines. Based on the results, they established a 4d CFD model [23,24]. Suceška evaluated fumes based on the thermodynamic calculations performed in Explo5 software as well as according to the BKW code [25]. Zawadzka-Małota has tested mining explosives concerning the content of carbon oxides and nitrogen oxides in their detonation products [26].

To decrease the migration of CO, Harris, and Mainiero suggested the application of negative pressure to a borehole by placing the drilling boom over an existing open hole near the blast site [27]. Silvester et al. studied particulate emissions from the open pit quarry [15].

Moreover, to determine the post-detonation properties of condensed-phase explosives some thermochemical computer codes like FORTRAN BKW, CHEETAH, EXPLO5, BARUT-X have been developed [27]. Thermochemical computer codes such as BKW, RUBY, TIGER, CHEQ, and CHEETAH, by assuming all of the chemical equations for all possible chemical compounds in the reaction fumes product and solving these with thermochemical analogs, can estimate the isentropic expansion having the equilibrium energy and gas quantities along with the Rankine–Hugoniot jump equations [6].

In 2003, Poland became part of The European Union. Following Directive 93/15/ECC, Poland, and other EU countries were obliged to design a uniform law, which included hazardous substances like toxic fumes [28]. The purpose of this law was to ensure the health and safety of the employees. This resulted in the creation of Polish Standard PN-EN 13631-16:2006, which focused on the cause of the concentration of toxic fumes, which are obtained throughout the detonation process [29]. The main aim of this paper is to present a fumes evaluation based on the most commonly used mining explosives such as Ammonium Nitrate Fuel Oil, dynamite, and emulsion. An emphasis is put on the general toxicity aspect.

2. General Toxicity

Because of the appearance of fumes, explosives materials are classified according to the corresponding countries' requirements. In Poland, the general toxicity limits of carbon monoxide and nitrogen oxides are set according to the following Equation (1).

$$L_{CO} = [X_{CO}] + k_{NO_2} [Y_{NO_x}] \quad (1)$$

where L_{CO} is general toxicity, $\text{dm}^3 \cdot \text{kg}^{-1}$; $[X_{CO}]$, $[Y_{NO_x}]$ is a volume of toxic fumes, $\text{dm}^3 \cdot \text{kg}^{-1}$; and k_{NO_2} is the toxicity coefficient.

The general toxicity expresses the sum of carbon monoxide and nitric oxide toxicity multiplied by the toxicity coefficient. The toxicity factor (k) expresses the ratio of the maximum permissible concentration of CO and maximum permissible concentrations of nitrogen dioxide.

In European Union countries that do not have either accredited measurement stations or European standards of toxic fume measurements, the controls of toxic oxides must be carried out directly at the workplace. In such cases, the toxicity factor determines the ratio of the maximum permissible concentrations (MPC) of carbon monoxide to nitrogen dioxide, which is expressed in Equation (2) [30]:

$$K_{NO_2} = [MPC_{CO}] \cdot [MPC_{NO_2}]^{-1} \quad (2)$$

where $[MPC_{CO}]$ is the maximum permissible concentration of carbon monoxide, and $[MPC_{NO_2}]$ is the maximum permissible concentration of nitrogen dioxide.

Following [31], the maximum concentration of oxides at the pit face must not exceed the value presented in Table 1 [31].

Table 1. The maximum permissible concentration of carbon monoxide [32].

Name of Oxide	MPC, mg/m^3
CO	23
NO ₂	3.5

The permissible concentration of toxic oxides, which determines the allowable explosive materials in various countries in underground mining is presented in Table 2.

In countries such as Finland, Netherlands, Romania, Sweden, United Kingdom, and Hungary, there are no strict criteria which limit the concentration of toxic fumes. The permissible concentration of oxides for underground ventilation is defined by each national legislation.

Since 2010, a tendency to move away from theoretically calculated values of general toxicity has been observed.

Based on Table 2, it can be observed that permissible concentrations of toxic fumes in Polish underground mines are, in the case of CO, no more than 0.135% by volume, which is $27 \text{ dm}^3 \text{ kg}^{-1}$, and for NO_x, no more than 0.080% by volume, which is $16 \text{ L} \cdot \text{kg}^{-1}$.

Table 2. The permissible concentration of toxic fumes in underground mining in various countries [33].

Country	Standard Requirements for an Amount of CO and NO _x
Belgian	No more than 50 dm ³ of CO and NO _x from 1 kg of explosive $L_{CO\ rel} = [X_{CO}] + 5[Y_{NO_x}]$
Bulgaria	No more than 100 dm ³ of CO and NO _x from 1 kg of explosive $L_{CO\ rel} = [X_{CO}] + 6.5[Y_{NO_x}]$
Czech	No more than 50 dm ³ of CO and NO _x from 1 kg of explosive $L_{CO\ rel} = [X_{CO}] + 6.5[Y_{NO_x}]$
France	No more than 50 dm ³ of CO and NO _x (as a sum) from 1 kg of explosive $L_{CO\ rel} = [X_{CO}] + 8[Y_{NO_x}]$
Spain	After the detonation process, the explosive material is given the following class: A—beneath 22.7 dm ³ CO and NO _x ·kg ⁻¹ of explosive. B—22.7 ÷ 46.7 dm ³ CO and NO _x ·kg ⁻¹ of explosive. C—above 46.7 dm ³ CO and NO _x ·kg ⁻¹ of explosive.
German	No more than 40 dm ³ of CO and 5 dm ³ of NO _x from 1 kg of explosive
Poland	No more than 27 dm ³ of CO and 16 dm ³ of NO _x were calculated per NO ₂ from a detonation of 1 kg of explosive No equation of general toxicity
Russia	No more than 50 dm ³ of CO and 5 dm ³ of NO _x from a 1 kg explosive $L_{CO\ rel} = [X_{CO}] + 6.5[Y_{NO_x}]$
Slovakia	No more than 50 dm ³ of CO and NO _x from 1 kg of explosive $L_{CO\ rel} = [X_{CO}] + 6.5[Y_{NO_x}]$
U.S.A.	No more than 100 dm ³ of CO. CO ₂ . NO. NO ₂ H ₂ S. SO ₂ (as a sum of gases) NO _x from 1 kg of explosive
Italy	No more than 60 dm ³ of CO and NO _x from 1 kg of explosive $L_{CO\ rel} = [X_{CO}] + 8[Y_{NO_x}]$

3. The Decomposition Products

The detonation process relies on the decomposition of molecular structures. Complex molecules decompose into simpler ones or single atoms. Based on the ideal model of the detonation process, reactants decompose into carbon dioxide, water vapor, and nitrogen. Reactants may also decompose into gaseous and other products, which did not decompose but underwent secondary reactions. In such cases, the products of the detonation process are carbon dioxide, carbon monoxide, nitrogen oxides, water vapor, and methane. In some cases, depending on the condition of the reaction, hydrogen may appear. Sulfur dioxide and hydrogen sulfide are not present in toxic fumes. Those products can appear only if blasting works are conducted in rock masses that contain sulfur. The same process can occur with lead and mercury.

Products of the detonation process that result from primary and secondary decomposition reactions can be explained by dividing the process of explosive detonation into two stages. During the first stage, a large increase in pressure results in a large volume of highly heated gases. This stage lasts until the rock mass, which surrounds the blasthole, starts to crack. In the second stage, rapid expansion occurs. Products from the first stage mix with air, which leads to cooling and secondary reactions. The main factor which results in the formation of toxic fumes is the oxygen balance. The excess or deficiency of oxygen may cause the formation of NO_x and carbon monoxide CO. It should be noted that these oxides may be formed in both stages of the reaction. In the primary reaction, during the explosion, and the secondary reactions. The secondary reaction and oxygen deficiency contribute to the formation of carbon monoxide. Based on the Kistiakovsky–Wilson rule, it can be seen that oxygen deficiency prevents the decomposition of carbon monoxide into carbon

dioxide. This incomplete oxidation causes an additional emission of CO. Certain quantities of carbon can react with water or carbon dioxide, according to Equation (3) [34]:



If the detonation process is completed, a reduction in carbon dioxide with hydrogen may occur, Equation (4):



Therefore, following Le Chatelier's Braun rule, an endothermic reaction results in an increasing amount of CO with increasing temperature and a decreasing amount of CO with increasing pressure.

After the detonation process, free carbon or carbon monoxide may react with the oxygen in the air according to Equation (5):



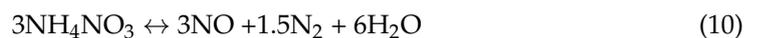
Another source of carbon monoxide formation is the ability of carbon to react with small amounts of carbon dioxide. This is a typical reaction for explosives which are characterized by oxygen deficiency. The reaction scheme is represented in Equation (6):



Often, methane is a byproduct of secondary reactions, as in Equations (7)–(9).



Nitrogen oxides are formed mainly from the incomplete decomposition of ammonium nitrate, as in Equation (10):



As a result of the incomplete decomposition of ammonium nitrate, obtained nitrous oxide undergoes a further violent explosive reaction. The reaction occurs at the time of detonation or after the decomposition. This results in a minimum concentration of nitrous oxide in toxic fumes. The reaction takes place according to Equation (11):



NO_x is formed during the incomplete decomposition of ammonium nitrate. Of all nitrogen oxides, the one produced in the largest quantities during the detonation process is nitric oxide. However, when it comes into contact with oxygen, nitric oxide oxidizes and converts to NO₂. This reaction is presented in Equation (12):



At a temperature of around 150 °C, nitrogen dioxide has a high tendency to associate, as demonstrated by Equation (13):



During the cooling process, the equilibrium of the reaction shifts to the right side (in the direction of dinitrogen tetroxide). This results in the presence of oxide in toxic fumes.

Fumes may include N₂O₃ and N₂O₅. However, due to their low toxicity and negligible concentrations, the reactions of their formation will not be discussed.

In addition to the primary and secondary reactions, the detonation of explosives can be followed by the afterburning effect. This means that in the case of the negative oxygen balance, the additional content of carbon monoxide, and soot which may be present in the composition of the post-blast fumes may interact with products of the decomposition reaction and lead to further increased detonation pressure [34]. In the research of Salzano and Basco, it was shown that the afterburning effect of the black powder decomposition products enables energy that is equal to the afterburning energy of TNT [35]. Moreover, the results of the afterburning effect were presented by [36].

4. Materials and Methods

4.1. Materials

Blasting tests were made for the explosives which were used in underground and open-pit mining.

In all tests, ANFO, emulsion, and dynamite charge in the form of a booster were researched.

In the case of ANFO, samples were produced by blending prilled ammonium nitrate(V) with fuel oil in a ratio 94:6. ANFO was placed in the glass tube. The diameter of the tube was 46 mm. The length of the tube was 750 mm. An exemplary charge is presented in Figure 1.



Figure 1. ANFO charge.

Ammonium nitrate(V) used in this research was of different prill sizes and absorption ratios. The absorption ratio was between 12 and 14%. Prill sizes were in the range of 7–8 mm. Prills of smaller diameter (higher absorption ratio) were used in ANFO samples: 4, 7, and 8.

In the case of emulsion explosives, the emulsion was placed in the polyethylene cartridge. The charge diameter was ca. 46 mm.

The general chemical composition of dynamite samples is presented in Table 3.

Table 3. Chemical compositions of researched dynamites.

Explosive	Dynamite Sample 1	Dynamite Sample 2	Dynamite Sample 3	Dynamite Sample 4
Ammonium nitrate(V)	71.29	53.8	N/A	58.0
Sodium nitrate(V)	-	10.0	N/A	4.0
Nitrocellulose	0.7	1.0	N/A	0.9
Nitroglycerine	13.2	16.8	N/A	16.2
Nitroglycol	8.8	11.2	N/A	10.8
Trotyl	-	3.0	N/A	-
Fuels	7.0	4.2	N/A	5.6
Modifiers	0.01	0.3	N/A	3.6

The chemical composition of dynamite sample 3 was not available.

Four types of emulsion bulk explosives were tested. An approximated chemical composition of emulsion bulk explosives is presented in Table 4.

Table 4. Chemical composition of tested emulsion explosives.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4
Organic component, %	5.5	4.2	4.8	5.3
Oxidizers, %	88.5	87.6	79.7	83.4
Water, %	4.0	3.2	15.6	7.1
Modifications, %	-	-	0.2	0.2
Aluminum powder, %	20	5.0	-	4.0

Emulsion sample 1, emulsion sample 2, and emulsion sample 4 were low-water composition (LWC) explosives.

4.2. Methods

The measurement of the volume of toxic fumes was obtained by the detonation of Polish explosives. Measurements were made according to [37]. Tests were carried out in the blasting chamber made of steel, Figure 2.

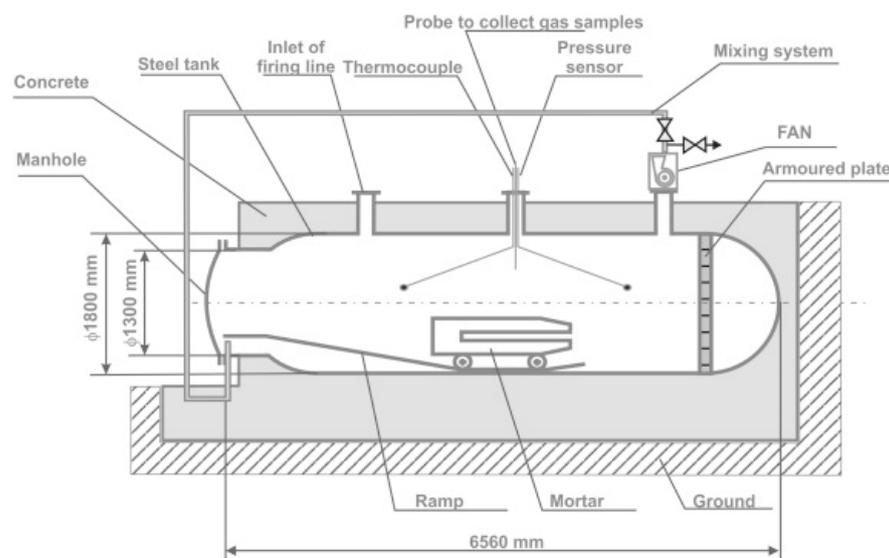


Figure 2. Blasting chamber [36].

The blasting chamber volume was 15 m³. The explosive booster was placed centrally in the mortar. The diameter of the borehole in the mortar was ca. 48 mm. Each explosive charge was initiated by the primer (cap-sensitive explosive in the form of the booster with a detonator). The RDX booster was armed with a single instantaneous electric detonator 0.2 A. After the decomposition, a 20 min measurement period begins. The blasting chamber is equipped with a mixing system combined with a fan system. The fan allows fume homogenization. The gas samples were collected automatically by the probe. From the probe, toxic fumes were transported along the cooling gas line to the analyzers. NO_x was measured by the TOPAZE 32M chemiluminescent analyzer. CO was evaluated based on the results obtained from MIR 25e, an infrared spectroscopy analyzer [37].

Assuming a gas-tight chamber, the concentrations of CO and CO₂, reach a constant value after the initial mixing period. The baseline concentration of NO_x oxides is obtained by extrapolating the dependence on concentration changes with time [37]. Each blasting was repeated 10 times per explosive type. Initially, obtained concentration values were averaged [37].

The construction of the chamber allows for multiple explosive detonations of an explosive mass of $450 \div 750$ g ($30 \div 50$ g of explosive per 1 m^3 of the chamber).

The velocity of detonation (VOD) was researched according to the standard in [38]. In terms of ANFO, the 600 g samples of non-ideal explosive charge were placed in a glass pipe. The pipe's inner diameter was 46 mm. Emulsion explosives and dynamite charges were in the form of boosters. In each test, a separate explosive charge was primed with 14 g RDX charge initiated by the electric detonator 0.2 A. VOD was measured by placing two short-circuit probes close to the top and bottom of the tube. The distance between the probes was 150 mm. The VOD was established by the division of the time difference which was derived by the progressing detonation with a distance between probes.

In terms of fumes and VOD tests, such an explosive sample was primed by the 14 g RDX-based booster armed with an instantaneous electric detonator.

5. Results and Discussion

Average concentrations of toxic oxides, VOD, and density ANFO samples are presented, respectively, in Tables 5 and 6. All calculations of general toxicity were made according to Equation (1).

Table 5. VOD and density of ANFO samples.

Explosive	Density	VOD
	g/cm^3	m/s
ANFO sample 1	0.829	2415 ± 27
ANFO sample 2	0.738	1678 ± 20
ANFO sample 3	0.733	1997 ± 25
ANFO sample 4	0.712	1282.5 ± 13
ANFO sample 5	0.707	1925 ± 27
ANFO sample 6	0.823	3140 ± 38
ANFO sample 7	0.746	1700 ± 22
ANFO sample 8	0.695	2024 ± 22

Table 6. Average fumes volume and general toxicity of various ANFO.

Explosive	The Amount of CO	The Amount of NO_x Calculated per NO_2	General Toxicity (L) k = 5	General Toxicity (L) k = 6	General Toxicity (L) k = 10
	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg
ANFO sample 1	17.50	10.70	71.00	81.70	124.50
ANFO sample 2	10.20	11.20	66.20	77.40	122.20
ANFO sample 3	16.20	9.40	63.20	72.60	110.20
ANFO sample 4	7.80	10.20	58.80	69.00	109.80
ANFO sample 5	6.00	12.40	68.00	80.40	130.00
ANFO sample 6	16.40	13.10	81.90	95.00	147.40
ANFO sample 7	15.00	10.2	66.0	76.20	117.00
ANFO sample 8	4.01	7.64	42.21	49.85	80.41
Average	11.63	10.61	64.66	75.27	117.69
STD, %	± 1.27	± 1.3	-	-	-

Based on Table 5, it can be observed that all tested ANFO samples had a VOD over 1000 m/s, which indicates that all samples detonated and further interpretation of fume results is relevant.

Based on Table 6, it can be concluded that the average concentration of NO_x is around $10.61 \text{ dm}^3 \cdot \text{kg}^{-1}$ and CO is around $11.63 \text{ dm}^3 \cdot \text{kg}^{-1}$. By taking into consideration Polish permissible levels of toxic fumes which are, respectively, 27 dm^3 and 16 dm^3 for CO and NO_x it can be stated that all tested samples did not exceed the permissible limit. Moreover, all examined explosives did not exceed the permissible limits of toxic fumes in other countries. However, if potential explosives applicability would be evaluated based on the permissible concentration which includes the general toxicity limits, the decision of

potential explosive applicability in various countries can be different. Table 2 indicates that depending on the toxicity coefficient (*k* index in the range of 5–10) by taking into consideration Equation (1) and Table 2, the difference in results depending on the *k* factor is ca. 50–65 dm³·kg⁻¹. For example, the biggest difference is in the case of sample 10 which is 65.50 dm³·kg⁻¹. This shows the potential ambiguity of the potential applicability in various markets.

Based on Table 6, it can be observed that the lowest volume of CO was calculated for samples 4, 7, and 8 (respectively 7.80, 15.00, and 4.01 dm³·kg⁻¹). Moreover, the same samples indicate the lowest NO_x volume, respectively, for sample 4: 10.20 dm³·kg⁻¹, for sample 5: 12.40 dm³·kg⁻¹, for sample 8: 7.64 dm³·kg⁻¹. This indicates that samples 4, 7, and 8 are close to the zero-oxygen balance. Furthermore, by taking into account that ANFO samples 4, 7, and 8 were based on the smaller prill size, it can be concluded that the surface of contact between the combustion agent and oxidant part is high, which influences the detonation process, especially by the possibility of the formation of the highest number of hot spots in comparison with the ANFO obtained based on the higher grade AN.

By comparison, fume volume (Table 6) derived from the detonation explosives that were produced between 2000 and 2010 (samples 1–5) compared with contemporary explosives (samples 6–8) showed no significant difference. The difference is strongly visible with the VOD. One of the factors which affects the VOD is the density of the explosive. It is well known that in a limited manner, the VOD rises with the density of the explosives. Based on Table 5, the linear relation is visible. However, it should be taken into account that ANFO is considered a non-ideal explosive. This means that VOD results that are obtained close to the ANFO’s critical diameter can vary significantly from the VOD obtained for the optimal explosive diameter.

Further tests were performed for a variety of the most commonly used water-in-oil (W/O) emulsion bulk explosives. In the W/O type of emulsion, a discontinuous water phase of inorganic oxidizer is dispersed in a continuous organic fuel phase. Droplets in the discontinuous phase are held in place by a proper W/O emulsifier [39]. The size of droplets is a key issue in emulsion properties, especially in the case of a highly concentrated emulsion [40]. In Tables 7 and 8, the basic emulsion explosives parameters such as density and VOD as well as average concentrations of emulsion bulk explosives are provided. All calculations of general toxicity were made according to Equation (1).

Table 7. VOD and density of emulsion samples.

Explosive	Density	VOD
	g/cm ³	m/s
Emulsion sample 1	1.101	3712 ± 45
Emulsion sample 2	1.060	3900 ± 66
Emulsion sample 3	1.096	3700 ± 42
Emulsion sample 4	1.060	4080 ± 41

Table 8. Average fumes volume and general toxicity of various compositions of emulsion bulk explosives.

Name of Explosive	The Amount of CO	The Amount of NO _x Calculated per NO ₂	General Toxicity (L) k = 5	General Toxicity (L) k = 6	General Toxicity (L) k = 10
	dm ³ /kg	dm ³ /kg	dm ³ /kg	dm ³ /kg	dm ³ /kg
Emulsion sample 1	9.10	5.40	36.1	41.50	63.10
Emulsion sample 2	9.80	4.60	32.8	37.40	55.80
Emulsion sample 3	19.80	4.20	40.8	45.00	61.80
Emulsion sample 4	10.20	5.40	37.2	42.60	64.20
Average	12.23	4.9	36.73	41.63	61.23
STD, %	±1.14	±1.19	-	-	-

The obtained results of general toxicity show a similar conclusion as in the case of ANFO. Based on Table 8, it can be observed that the average concentration of NO_x is around $4.9 \text{ dm}^3 \cdot \text{kg}^{-1}$ and CO is around $12.23 \text{ dm}^3 \cdot \text{kg}^{-1}$. By taking into consideration Polish permissible levels as well as other nationally permissible levels, it can be stated that tested emulsion explosives samples did not exceed the permissible limits. In the case of general toxicity, the maximum difference between the samples was ca. $27.0 \text{ dm}^3 \cdot \text{kg}^{-1}$ in emulsion samples 1 and 4. The difference is much lower in comparison with ANFO. This can be explained by the low differences in NO_x volume between emulsion samples. The low volume of NO_x fumes amplifies the fact that emulsion explosives are the most ecologically friendly type of explosives in the mining industry.

Based on Table 8, the highest volume of CO was observed for emulsion sample 3 ($19.80 \text{ dm}^3 \cdot \text{kg}^{-1}$). This can be explained by the chemical composition of explosive material. Emulsion explosive sample 3 had the highest content of organic components up to c.a. 6.0% in comparison with other emulsion samples (fuel component in the range of $4.2 \div 5.5\%$). By taking into consideration the modified Kistiakowski–Willson rule or Springall–Roberts rule, the first phase of decomposition is the oxidation of carbon atoms to carbon monoxide. Moreover, emulsion explosives samples 1, 2, and 4 were low-water-composition explosives that were characterized by a water content of up to 7%. In terms of regular emulsion explosives, water content is on average 15%. The higher content of water influences the heat of detonation and VOD. Usually, LWC explosives have a higher heat of detonation and VOD values. Based on Table 7, it can be observed that low-water-composition emulsions (samples 1, 2, and 4) had a higher VOD in comparison to emulsion explosive sample 3, respectively, 3710, 3900, 4080 m/s to 3700 m/s. The high VOD in terms of sample 3 and sample 4 can also be explained by the addition of aluminum powder (respectively, 4 and 5%), which increased the heat of the explosion.

Besides ANFO and emulsion bulk explosives, one of the most popular explosive types that is applied in the mining industry is dynamite. The results of density, general toxicity, and toxic fumes are presented in Tables 9 and 10. All calculations of general toxicity were made according to Equation (1).

Table 9. VOD and density of dynamite samples.

Explosive	Density	VOD	Oxygen Balance
	g/cm^3	m/s	%
Dynamite sample 1	0.829	2415 ± 24	+6.64
Dynamite sample 2	0.738	1678 ± 20	+7.81
Dynamite sample 3	0.733	1997 ± 26	+3.62
Dynamite sample 4	0.712	1282.5 ± 13	+5.53

Table 10. Average fume volume and general toxicity of various compositions of dynamite explosives.

Name of Explosive	The Amount of CO	The Amount of NO_x Calculated per NO_2	General Toxicity (L) k = 5	General Toxicity (L) k = 6	General Toxicity (L) k = 10
	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg
Dynamite sample 1	15.67	15.2	91.67	106.87	167.67
Dynamite sample 2	16.4	10.0	66.40	76.40	116.40
Dynamite sample 3	22.31	12.27	83.66	95.93	145.01
Dynamite sample 4	23.93	12.53	86.58	99.11	149.23
Average	19.58	12.50	82.08	94.58	144.58
STD, %	± 1.08	± 1.09	-	-	-

Based on Table 10, it can be observed that dynamite sample 4 has the highest volume of CO ca. $23.93 \text{ dm}^3/\text{kg}$. This can be explained by the chemical composition of the explosive sample. In the case of sample 4, the combustible components (fuels, modifiers, an TNT) consist of the larger part of the dynamite chemical composition (ca. 9.2%). It can be assumed

that dynamite sample 3 has a similar chemical composition to dynamite sample 4. In the case of dynamite sample 1 and sample 2, the combustible components consist, respectively, of ca. 7.01% and 7.5%. This results in a similar volume of CO. In terms of NO_x, it can be observed that dynamite sample 1 has the highest volume of nitrous fumes. This partially corresponds with the oxygen balance (6.64%, Table 9). Normally, with higher positive values (oxygen balance), more NO_x appears. By taking into consideration Table 9, the highest oxygen balance can be observed with dynamite sample 2 which corresponds with the lowest volume of NO_x. However, based on the chemical composition of the explosives, it can be observed that despite the oxidizing agents consisting of similar parts of the explosive, the main difference stems from sodium nitrate. Dynamite sample 2 consists of the highest content of this oxidizing agent ca. 10%. Other samples have a lower content of sodium nitrate(V) which causes there to be additional nitrogen atoms in the chemical composition which influences decomposition products (NO_x and N₂).

Based on the general toxicity, it can be concluded that all tested samples meet Polish and other national standards. However, if we take into consideration different toxicity coefficients, it can be observed that the difference between general toxicity values reaches up to ca. 76.0 dm³/kg (dynamite sample 1). The large variance between results leaves room for inaccurate interpretation.

An average volume of toxic fumes of all types of explosives is presented in Table 11.

Table 11. Average fumes volume and general toxicity of tested ANFO, emulsion explosives, and dynamites.

Name of Explosive	The Amount of CO	The Amount of NO _x Calculated per NO ₂	General Toxicity (L) k = 5	General Toxicity (L) k = 6	General Toxicity (L) k = 10
	dm ³ /kg	dm ³ /kg	dm ³ /kg	dm ³ /kg	dm ³ /kg
ANFO	11.63 ± 1.27%	10.61 ± 1.30%	64.66	75.27	117.69
Emulsion	12.23 ± 1.14%	4.90 ± 1.19%	36.73	41.63	61.23
Dynamite	19.58 ± 1.08%	12.50 ± 1.09%	82.08	94.58	144.58

Based on Table 11, it is noted that the explosives which were tested meet the standards for civilian use. ANFO has a low concentration of nitrogen oxides. The concentration of NO_x is comparable in value with the concentration of carbon monoxide produced by the ANFO detonation. This is due to the chemical composition of the explosive. The dominant component is highly porous ammonium nitrate. Oxygen balance and ammonium nitrate are responsible for the formation of NO_x. Carbon oxides are the product of the decomposition of the organic part, which comprises only a small percentage of the total weight of the product. This is the reason why the concentration of carbon monoxide is low.

Furthermore, it must be noted that emulsion bulk explosives are the most environmentally friendly.

6. Conclusions

Based on the obtained results, it can be concluded that an evaluation methodology simulates typical conditions of blasting works and allows for research of various types of explosives. However, the mortar diameter is close to the critical diameter of non-ideal explosives, which can have a significant influence on results. In the future, the construction of the mortar could be improved.

Results of fume analysis performed according to the standard in [34] are extremely important in terms of the application of explosives in underground mines. The preliminary results indicate the potential influence of fumes on the miners' working conditions and influence work safety.

Based on the results it can be stated that all tested explosives comply with the standards for different permissible levels of toxic oxides. The lowest concentration of fumes (NO_x) occurs in emulsion explosives. It is caused by a very large surface of contact between the oxidant and organic phase. Also, an oxygen balance that is close to 0 is highly recommended.

However, the significant amount of CO in emulsion explosives can be explained by the polyethylene cartridge which also takes a part in the decomposition reaction.

Explosive materials, which have an oxygen balance from 0 to 5% are characterized by the least amount of toxic gases and the greatest strength of detonation. This is the reason why manufacturers strive towards these types of materials.

The formula for general toxicity has different characteristics in different EU countries or in the U.S. Due to the possible toxicity coefficient (k) in the range of 5 to 10, or the maximal permissible volume of fumes, it is noted that—assuming different values—the same explosive material can obtain varying compartment results. From this, it follows that the same explosive material, in some countries, can have a general toxicity value over the permissible level. It is possible to notice a slow trend of neglecting the general toxicity coefficient in EU standards. However, coefficient unification should be recommended. Future work should focus on the design of unified permissible levels of fumes.

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