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Testing of mining explosives with regard to the content of carbon oxides and nitrogen oxides in their detonation products

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ABSTRACT

Blasting operations are a risk to the lives of mining workers. Blasting gases are particularly dangerous factors – these are the products from detonations which come from applying explosives which contain toxic nitrogen oxides and carbon monoxide. The aim of this study was the experimental determination of the composition of the blasting gases from a variety of explosives currently being produced in Poland. On the basis of research results, analysis was carried out. To perform research of the composition of blasting gases, after the detonation of explosives, a laboratory test stand was used. The study involved the determination of gaseous products, i.e. nitrogen oxides and carbon oxides. Research was carried out in accordance with research methodology based on European Directive 93/15/EEC and the harmonized standard PN-EN 13631-16. These studies provided information on the amount of harmful gaseous products from mining explosives after detonation.

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1. Introduction

During detonation, explosives used in mining undergo rapid decomposition due to high temperatures and large amounts of constantly evolving gases and heat. The more gases accompanying the decomposition of explosives, the higher the pressure of the gases in the blast hole. Therefore, the results of such blasting operations are greater. Additionally, gases that evolve during the detonation process contain gaseous products which are highly hazardous, such as: carbon monoxide CO, nitrogen monoxide NO and nitrogen dioxide NO₂ (their molecular formulae are marked as NO_x). In addition to these oxides, another significant impact of blasting techniques is the release of the non-toxic gas carbon dioxide CO₂,

which is the product of the final explosive transformation of explosives (Mainiero, Harris, & Rowland, 2007).

During explosive transformation, alteration of the chemical structure of the explosive takes place. Decomposition of the initial molecular structure of the explosive leads to the creation of a non-equilibrium chemical system wherein reactions occur between atoms, radicals and products of the partial decomposition of materials. The primary source of energy from explosions, using an explosive that has a typical elemental composition C_aH_bN_cO_d, is the energy discharged during the formation of water molecules H₂O and carbon dioxide CO₂ (Maranda, Cudzito, Nowaczewski, & Papiński, 1997; Badgujar, Talawar, Asthana, & Mahulikar, 2008).

Toxic oxides are formed during basic explosive reactions between nitrogen, oxygen and carbon. These transformations

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relate closely to the oxygen balance, which is expressed as a percentage of the difference between the amount of oxygen contained in the explosive and the amount of oxygen that is essential to complete the oxidation of carbon to carbon dioxide and hydrogen to water (Urbański, 1985; Agrawal, 2010). The oxygen balance is indicated as positive, zero or negative when the oxygen content in the explosive is, respectively, bigger than, equal to or smaller than the amount of oxygen required to complete combustion of carbon and hydrogen to carbon dioxide and water.

The chemical reactions which lead to the formation of detonation products, including carbon monoxide CO and nitrogen oxides NO_x, were discussed in literature many years ago (Szepieliev & Kustov, 1974).

Taking into account that detonation products depend both on their chemical composition and the conditions in which detonation occurs, precise information as to the composition of blasting gases can be obtained from experimental tests.

This paper presents the research of selected cartridge explosives intended for use in underground mining. For these explosives there is a requirement to determine the composition of the blasting gases that are formed after their detonation. The explosives tested were produced by a leading Polish industrial explosive company.

Firing of the prepared charges were made for each explosive selected. During the firing of the explosives, the content of nitrogen monoxide NO and nitrogen dioxide NO₂ (referred to as NO_x), carbon monoxide CO (as toxic gases) and carbon dioxide CO₂ was determined. The research results concerning the composition of blasting gases for each explosive were obtained for several different batches of production. Their mean values were compared with the boundary values of the aforementioned oxides on the basis of criteria established in Poland and other European countries.

2. Methods and material

2.1. Explosive characteristics

The research subject matter consisted of materials which belong to two groups:

- Rock explosives (ammonites, dynamites, emulsion explosives) which do not correspond to the requirements concerning mixtures of methane and/or coal dust and air as

defined in the Polish standard (PN, 1997) during safety tests, special methane explosives – permitted explosives (methanite) which correspond to the requirements defined in the standard above during safety tests with a mixture of methane and/or coal dust and air.

- Tested explosives i.e. ammonites (Ammonite 1, Ammonite 2) and one methanite (Methanite 1), according to Polish classifications due to their structure and chemical composition, belong to the subgroup of ammonium - nitre powdery explosives. Dynamites (Dynamite 1, Dynamite 2, Dynamite 3, Dynamite 4), on the other hand, belong to the subgroup of nitrate ester plastic explosives. All of the explosives mentioned are varieties of explosives devoid of carcinogenic nitro compounds i.e. dinitrotoluene and trinitrotoluene.

The emulsion explosives are the most recent variety of explosives used in mining. Their basic components include oxidizing agents. The most common of which is ammonium nitrate which is also in a mixture with either sodium nitrate or calcium nitrate. Other components include fuels, water, emulsifiers, allergenic and modifying agents. Tested emulsion explosives (MWE 1, MWE 2, MWE 3) belong to the group of rock explosives. Table 1 shows the summary and characteristic of the tested explosives.

The detonators which contained 0.6 g of penthrite as a secondary charge were used to initiate the detonation of the explosives highlighted.

2.2. The research method

The determination of the composition of blasting gases was carried out in accordance with the requirements of European standard (PN-EN, 2006). The above-mentioned standard is harmonized with the directive (93/15/EEC, 1993) which specifies the blasting gases research method. However, it does not include the requirements with regards to acceptable amounts of toxic carbon monoxide CO and nitrogen oxides NO_x for 1 kg of explosive detonated. Therefore, each country applies its own rules and normative requirements in this field.

In order to carry out the determination of the composition of blasting gases, the charges were made of explosives mentioned in Section 2.1 and initiators. Charges were detonated in a blast chamber as shown in Fig. 1. The chamber consisted of classic steel mortar. The detonation of the charges was carried out on the test bench designed for

Table 1 – The summary and characteristic of the tested explosives.

Explosive	Charges diameter [mm]/mass [g]	Charge shield	Explosive structure	Type of explosive	Oxygen balance
Ammonite 1	32/125	Paper	Powdery	Rock	+1.8
Ammonite 2	32/125	Paper	Powdery	Rock	+2.9
Dynamite 1	36/450	Polyethylene	Plastic	Rock	+4.2
Dynamite 2	32/300	Paper	Plastic	Rock	+3.3
Dynamite 3	40/1000	Polyethylene	Plastic	Rock	+2.6
Dynamite 4	50/500	Polyethylene	Plastic	Rock	+8.44
MWE 1	40/750	Polyethylene	Plastic	Rock	+8.7
MWE 2	32/300	Polyethylene	Plastic	Rock	+8.65
MWE 3	40/750	Polyethylene	Plastic	Rock	-2.38
Methanite 1	32/125	Paper	Powdery	Methanoic special	+4.4

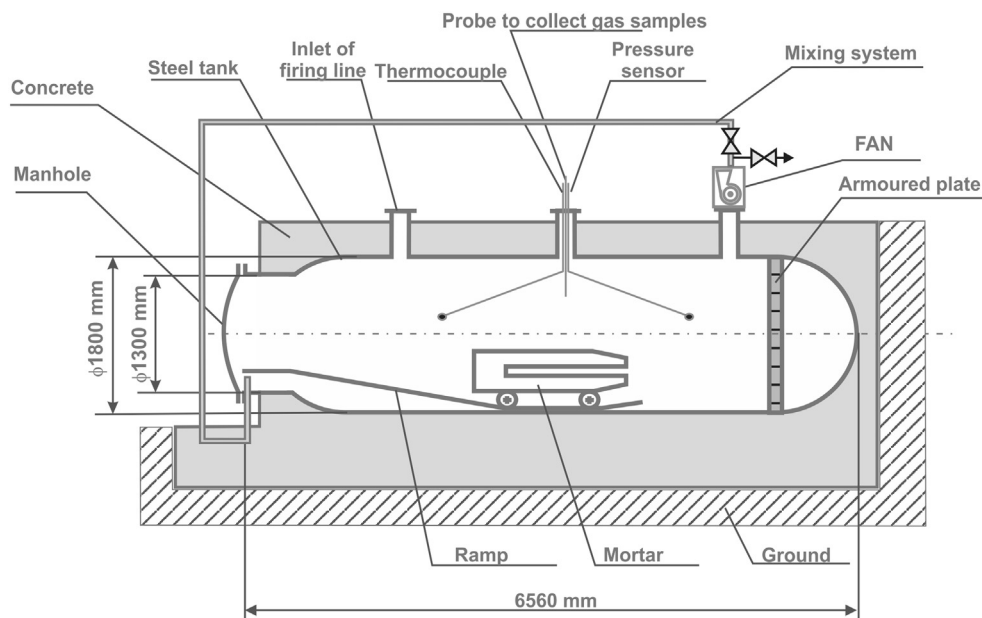


Fig. 1 – The scheme of the 15 m³ capacity blasting chamber with circulation system.

blasting gas research, which is located in the Explosives and Detonators Research Laboratory, Experimental Mine “Barbara” at the Central Mining Institute.

An essential element of the test bench is the blasting chamber equipped with an integrated mixing and ventilation system used for atmosphere homogenization after the detonation of explosives and for the removal of detonation products after the completion of the research.

Simultaneously, when firing each explosive charge, the registration of nitrogen oxides NO_x, NO, NO₂ and carbon oxides CO, CO₂ concentrations in samples was carried out. However, samples used for analysis were taken from the mixed atmosphere in the blasting chamber, wherein gases underwent cooling and pressure underwent equalization after the explosion.

The content of oxides: NO_x, NO, NO₂, CO and CO₂ in blasting gases was measured for 20 min using two constant measurement analysers. An infrared technique was used to measure CO and CO₂ (IR analyser MIR 25 – Environnement, France) and a chemiluminescent analyser was used for NO and NO₂ (TOPAZE 32 M – Environnement, France).

3. Results and discussion

The mean concentration values of oxides: CO, CO₂, NO, NO₂, NO_x from the measurements of three detonations of each of the explosives was determined. The amount of each oxide was calculated in litres per kilogramme of explosive.

On the basis of the results of the amount of carbon monoxide CO and nitrogen oxides NO_x, relative general toxicity was estimated. This parameter presents the total amount of carbon monoxide CO and nitrogen oxides NO_x multiplied by the general toxicity factor of 6.5 (Szepieliev & Kustov, 1974).

Relative general toxicity (L_{co}) is described using the following equation:

$$L_{co} = CO + 6.5 \times NO_x \tag{1}$$

where:

CO – the amount of carbon monoxide [l/kg].

NO_x – the amount of nitrogen oxides [l/kg].

Relative general toxicity parameter estimations for blasting gases is are required in some European countries (Zawadzka-Małota & Sobala, 2007). The mean values of carbon oxides, nitrogen oxides and general relative toxicity are presented in Table 2.

Fig. 2 and Fig. 3 show the results of explosive decomposition, i.e.: carbon oxides CO, CO₂ and nitrogen oxides NO_x. Fig. 4 shows the amount of the determined toxic nitrogen oxides NO_x and carbon monoxide CO.

Fig. 4 also presents the determined nitrogen oxides NO_x and carbon monoxide CO boundary values in underground usage explosives in accordance with Polish requirements

Table 2 – The results of the determination of the composition of explosives' blasting gases – the amount of carbon oxides, nitrogen oxides and general relative toxicity.

Explosive	The amount of oxides [l/kg]					
	CO ₂	CO	NO	NO ₂	NO _x	CO + 6.5 × NO _x
Ammonite 1	145.15	5.87	3.58	1.15	4.74	36.65
Ammonite 2	110.22	2.63	0.77	0.56	1.22	10.56
Dynamite 1	167.45	5.93	0.92	0.07	0.99	12.38
Dynamite 2	181.60	4.37	2.61	4.50	0.64	8.53
Dynamite 3	185.12	4.58	1.89	0.11	2.00	17.59
Dynamite 4	171.53	1.56	5.49	0.46	5.96	40.31
MWE 1	109.34	21.85	0.62	0.06	0.68	26.28
MWE 2	123.72	21.43	1.09	0.06	1.15	28.90
MWE 3	105.26	21.43	0.38	0.02	0.40	24.03
Methanite 1	91.85	9.29	3.69	0.16	3.86	34.35

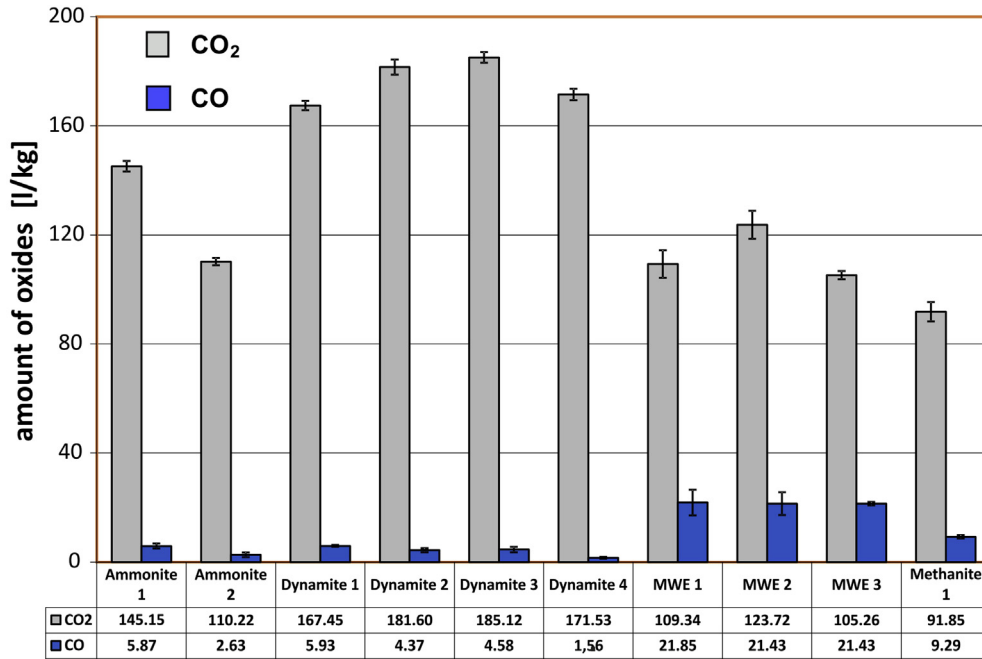


Fig. 2 – Mean values of determinate amounts of carbon oxides CO and CO₂ in explosives' blasting gases.

which amount to: 16 L of NO_x per kilogramme of explosive and 27 L of carbon monoxide CO per kilogramme of explosive (PN, 1997).

In order to assess whether the explosives researched meet the requirements of general relative toxicity parameter, which amounts to a maximum of 50 L of gas per 1 kg of explosive and is adopted in such European countries as Slovakia, the Czech Republic, Belgium and France (Zawadzka-Małota, 2008). Fig. 5

presents an estimation which is relative to the boundary value.

The data in Table 2 and Figs. 2–5 present different amounts of carbon oxides CO, CO₂ and nitrogen oxides NO, NO₂, NO_x in the detonation products of each explosive. The reason for this is different chemical compositions (also oxygen balance), chemical structures, formulation and type of explosive charge shields researched.

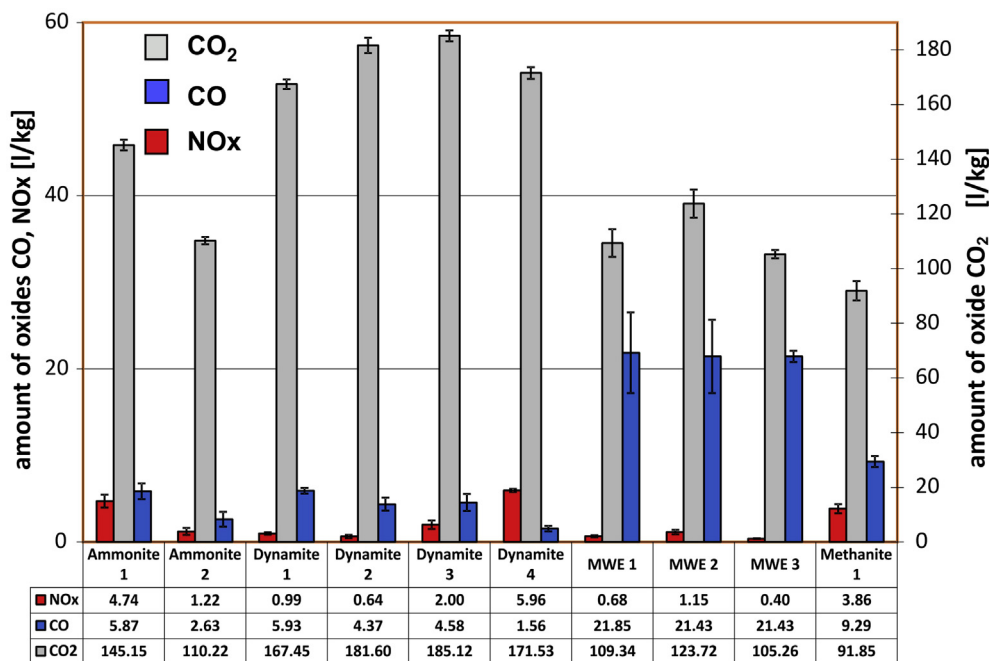


Fig. 3 – Comparison of the results of carbon oxides CO, CO₂ and nitrogen oxides NO_x presented in Table 2.

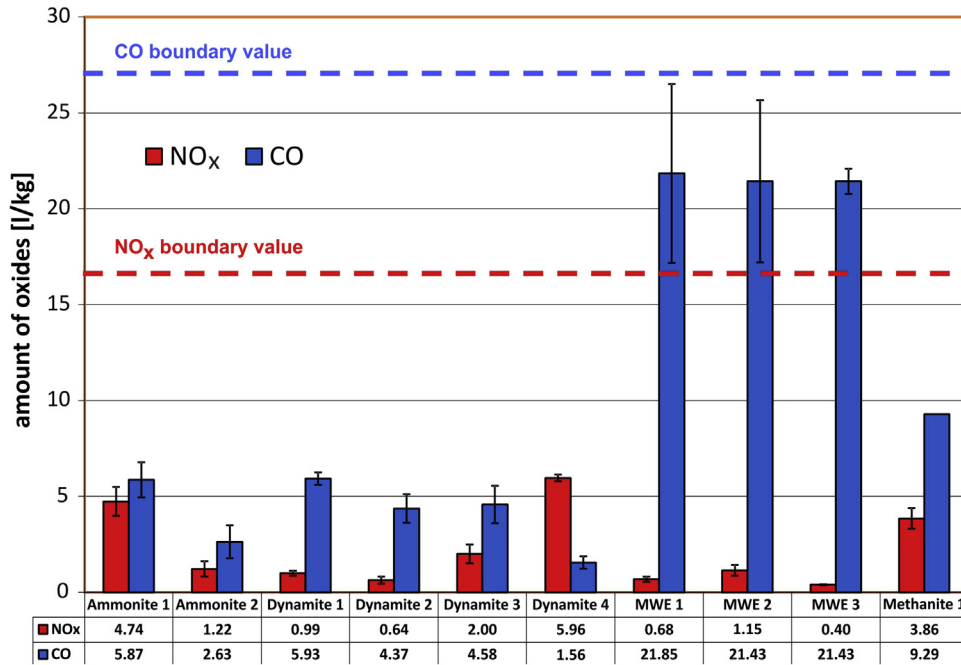


Fig. 4 – Presentation of the mean values of carbon monoxide CO and nitrogen oxides NO_x in explosives blasting gases with regard to the boundary values required in Poland.

If the chemical reaction of a detonation led to the complete decomposition of the explosive, only nitrogen N₂, carbon dioxide CO₂, water vapour H₂O and oxygen O₂ would be present in gas products. Due to the fact that mining explosives are heterogeneous mixtures, diagnosis of the chemical

processes that occur during a chemical explosion is a highly complex task. The formation of detonation products occurs under conditions of high pressures and temperatures, as well as in the cooling phase of products capable of further reactions.

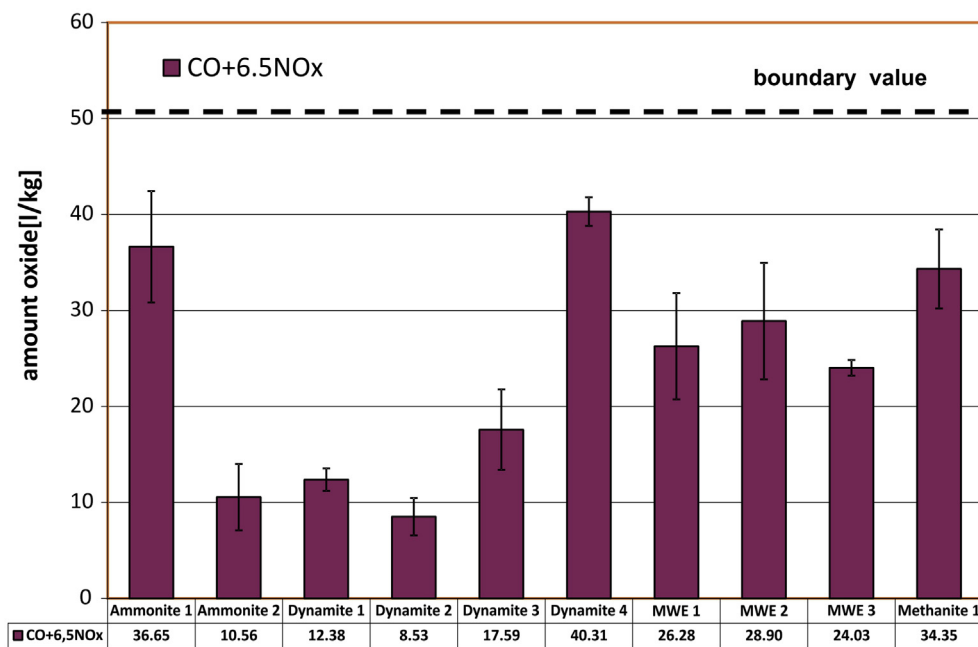


Fig. 5 – General relative toxicity estimated on the basis of determinate amounts of carbon monoxide CO and nitrogen oxides NO_x in explosives' blasting gases.

4. Conclusion

By analysing the test results for the ten explosives used in Polish mining, the following conclusions were made:

Experimental determination of the quantitative and qualitative features of the composition of blasting gases provides an insight in to the course of the explosives' decomposition reaction.

The detonation products of each explosive contain toxic nitrogen oxides NO_x , toxic carbon monoxide CO and carbon dioxide CO_2 .

The largest amount of carbon monoxide CO in blasting gases is typically found in emulsion explosives: MWE 1, MWE 2, MWE 3 cartridge in polyethylene. However, small amounts of toxic nitrogen oxides NO_x , occur in the detonation products of these explosives.

A significant amount of carbon dioxide CO_2 , i.e. the final detonation process product, occurs in explosives' detonation products (particularly in the case of: Dynamite 1, Dynamite 2, Dynamite 3 and Dynamite 4).

None of the tested explosives exceeded the threshold of the amount of nitrogen oxides NO_x (16 L per kilogramme of explosive) or the threshold of the amount of carbon monoxide CO (27 L per kilogramme of explosive). These boundary amounts are determined by Polish requirements for explosives designed for use in underground mining.

On the basis of the estimated general relative toxicity, it can be stated that the explosives researched meet the requirements in some European countries, i.e. they do not exceed the boundary value of general relative toxicity that amounts to 50 L of gas per kilogramme of explosive.

The results of the research concerning the composition of explosives' blasting gases is highly useful in blasting operations in underground mining and surface mining as well as providing safer working conditions for employees and environmental protection.

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