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Investigation of gaseous combustion products of pyrotechnic gas generators "ROCKSPLITTER™"
Badanie gazowych produktów spalania pirotechnicznego urządzenia gazogenerującego typu ROCKSPLITTER

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Abstract: *Gas generating devices utilising the decomposition of pyrotechnic mixtures can be an alternative to those containing high explosives – whose purpose is the splitting of rock. Large volumes of gas at high temperature and pressure can cause the splitting of blocks from virgin rock.*
Comparison of the composition of gas products of the gas generator ROCKSPLITTER™ with those of the detonation products of the alternative, penthrite detonating cord for rocks, has been carried out within the framework of this investigation. The determination of the composition of the gases was carried out at the Laboratory of Explosives and Electric Detonators Testing, at Experimental Mine „Barbara" of the Central Mining Institute (Mikołów, Poland) at the experimental facility established for determining gaseous detonation products of blasting explosives. Testing was performed in accordance with the modified test method described in European Standard PN-EN-13631-16:2006P, "Explosives for civil uses. High explosives. Detection and measurement of toxic gases".
Streszczenie: *Alternatywnym rozwiązaniem dla urządzeń zawierających kruszące materiały wybuchowe i służących do odspajania bloków skalnych mogą być urządzenia (wyroby) gazogenerujące w wyniku działania których następuje rozkład mieszanin pirotechnicznych. Podczas rozkładu substancji pirotechnicznych powstają duże ilości gazów o wysokiej temperaturze i ciśnieniu zdolnych do odspajania bloków skalnych od calizny.*
W ramach pracy wykonano badanie składu gazowych produktów spalania pirotechnicznego wyrobu gazogenerującego ROCKSPLITTER oraz porównano je ze składem produktów detonacji alternatywnie użytego skalnego lontu detonującego pentrytowego. Badanie składu gazów wykonano w Laboratorium Badań Materiałów Wybuchowych i Zapalników Elektrycznych przy Kopalni Doświadczalnej „Barbara" w Głównym Instytucie Górnictwa w Mikołowie na stanowisku badawczym do oznaczania gazowych produktów detonacji górniczych materiałów wybuchowych. Badanie to wykonano modyfikując metodę opisaną w Normie Europejskiej PN-EN-13631-16:2006P pt. „Materiały wybuchowe do użytku cywilnego. Materiały wybuchowe kruszące. Wykrywanie i oznaczanie gazów toksycznych".

Keywords: *pyrotechnic gase generators, explosives, post-blast gases*
Słowa kluczowe: *urządzenia gazogenerujące, materiały wybuchowe, gazy postrzałowe*

1. Introduction

Gas generators traded as ROCKSPLITTER™, are pyrotechnic devices which belong in the P1class under "other pyrotechnical items" [1]. They are designated for quarrying including: the splitting of rock, eliminating oversizing stones, as well as other blasting work, *e.g.* demolition.

These devices are constructed as cylindrical charges consisting of a pyrotechnic substance (oxidizer) and diesel oil (fuel) mixed immediately prior to use [2]. At that moment, they are classified asP2 class, meaning their use is permitted by „a person with specialist knowledge" *e.g.* a shot-firer.
During decomposition of the pyrotechnic substances, large quantities of gas are produced. Because of the high temperatures and pressures, these gases are able to split blocks out of virgin rock.
The temperature range at which ROCKSPLITTER™ gas generators are used is between -20 °C and +30 °C. They can be loaded into dry blast holes with diameters varying from 28 mm to105 mm. Loading into wet holes is possible only after removing water from such holes.
During the decomposition reaction of the pyrotechnic mixtures in the devices very small quantities of solids and relatively large quantities of gaseous compounds of nitrogen (N) and carbon (C)are formed, among others. Finally, decomposition reaction causes the formation of toxic nitrogen oxides NO and NO_2 as well as carbon monoxide CO, which negatively influence the natural environment [3].
It is known that there is more than one analytical method which can be used in determining the composition of gases obtained from the burning of pyrotechnic mixtures present in gas generators. Frequently, more than one method needs to be used as described elsewhere, [4-7].
Within the frame work, testing was carried out in accordance with CEBAR-DG Company orders, to determine the composition of gaseous combustion products of the ROCKSPLITTER™ gas generators as well as comparing the results with those of the alternative, penthrite detonating cords for rocks. Determination of the composition of the gaseous products was carried out in the Laboratory of Explosives and Electric Detonators Testing, at the Experimental Mine „Barbara" of the Central Mining Institute in Mikołów at the facility established for determining gaseous detonation products of blasting explosives [8].

2. Materials and methods

2.1. Testing of gaseous combustion products of pyrotechnic item ROCKSPLITTER™

In order to determine the composition of the gaseous products of ROCKSPLITTER™ one has to carry its combustion in a tightly closed detonation chamber. The composition of the gases produced was carried out using an analyzer dedicated to the continuous measurement of carbon oxides: CO, CO_2 using an infrared monitoring technique (IR-analyzer MIR 25, Environnement - France) with a chemiluminescence analyzer for continuous measurement of nitrogen oxides: NO, NO_2 and the total NO_x (TOPAZE 32 M analyzer, Environnement - France) [8, 9].
Additionally, an Agilent Technologies 6890 N gas chromatograph was applied in the determination of composition of the gaseous combustion products.

2.1.1. Determination of chemical composition of gaseous combustion products of ROCKSPLITTER™

Combustion of ROCKSPLITTER™ pyrotechnical items were carried out in accordance with the modified test method described in European Standard PN-EN-13631-16:2006P and focused on the detection and determination of toxic gases [10].
Three ROCKSPLITTER™ devices were tested. Each was placed in a steel pipe. The pipe was inserted into the opening of a steel mortar positioned inside a detonation chamber with a volume of 15 m^3. Electric wires of the ROCKSPLITTER™ ignition system (each device has its own initiation system) were connected to an exploder. The exploder is dedicated for the initiation of this kind of pyrotechnic charge.
In order to determine the composition of the combustion gases present after ignition of the ROCKSPLITTER™ charge, the gases in the detonation chamber (CO, CO_2, NO, NO_2 and NO_x) were sampled continuously over a period of 20 min. Gas chromatography analysis was applied in determining the devices' combustion products of hydrogen (H_2) and unsaturated hydrocarbons: ethene (C_2H_4) and saturated hydrocarbons: methane (CH_4) and ethane (C_2H_6).

2.1.2. Results

Initiation of the ROCKSPLITTER™ device was accompanied by both aloud sound and the release of large amounts of smoke. In all three trials, it was noted that all polymeric components of the ignited charges were totally burnt out. In Fig. 1, a tested ROCKSPLITTER™ device, after burning out of its pyrotechnic mixture, is shown (confinement was open at both sides).

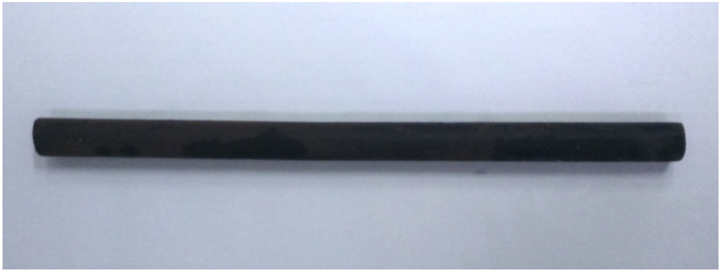

Fig. 1. Appearance of ROCKSPLITTER™ device after burning out of its pyrotechnical mixture.

Average values of three determinations of oxide concentrations: CO, CO_2, NO, NO_2, and NO_x, expressed in ppm, %V/V and litres per kilogram of ROCKSPLITTER™ composition (L/kg) are presented in Table 1.

Table 1. Results of oxides content: CO, CO_2, NO, NO_2, NO_x after burning out of ROCKSPLITTER™ device

Average values after burning out of three ROCKSPLITTER™ charges	**CO_2***	**CO***	**NO***	**NO_2***	**NO_x***
Concentration of gase [ppm]	1289.104	505.736	6.769	1.302	8.072
Concentration of gase [%]	0.129	0.051	0.001	0.000	0.001
Volume of gase [L/kg]	**61.32**	**24.07**	**0.32**	**0.06**	**0.38**

** - extrapolation of concentration to time t = 0 min (ignition of the pyrotechnical device)*

Average values for the three determinations carried out using gas chromatography of other gaseous combustion products expressed in ppm, %V/V and litres per kilogram of pyrotechnical item (L/kg), are shown in Table 2. Hydrogen and unsaturated hydrocarbon, *i.e.* C_2H_4, were detected and their concentrations were determined. Analysis did not confirm the presence of saturated hydrocarbons, *i.e.* CH_4 and C_2H_6.

Table 2. Results of gaseous combustion products after burning out of ROCKSPLITTER™ device, using gas chromatography

Average values after burning out of two ROCKSPLITTER™ charges	**H_2****	**CH_4****	**C_2H_4****	**C_2H_6****
Concentration of gase [ppm]	235	-	207	-
Concentration of gase [%]	0.0235	-	0.0207	-
Volume of gase [L/kg]	**3.83**	**-**	**3.38**	**-**

*** - average value of determination for time t = 10 min of duration of combustion*

2.2. Testing of gaseous detonation products of penthrite detonating cord for rocks

Testing of gaseous products of detonation of penthrite detonating cord for rocks (containing 20 g PETN per linear meter) was carried out in the in the detonation chamber, following detonation of the item. The analysis was carried out using an analyzer dedicated to continuous measurement of carbon oxides (CO and CO_2), by an infrared monitoring technique(IR-analyzer MIR 25, Environnement - France), as well as a chemiluminescence analyzer for continuous measurement of nitrogen oxides: NO, NO_2 and their total NO_x (TOPAZE 32 M analyzer, Environnement - France).

Additionally, an Agilent Technologies 6890 N gas chromatograph was applied for analysis of the composition of gaseous detonation products.

2.2.1. Determination of chemical composition of gaseous post-blasting products of penthrite detonating cord for rocks

Initiation of charges prepared from segments of the penthrite detonating cord were carried out in the same experimental facility where the determination of the composition of combustion products of ROCKSPLITTER™ was performed.
Three segments of penthrite detonating cord, each of 1 m length, were prepared for the tests. Each segment was initiated by methane safe instantaneous electric detonator, containing a 0.6 g mass of PETN secondary charge. A segment of the cord was inserted into the hole in the mortar inside the detonation chamber and initiated as previously.
In order to determine the composition of gases present after detonation of the cord, the atmosphere in the detonation chamber was sampled continuously over a period of 20 min, to analyse CO and CO_2 as well as NO, NO_2 and the total NO_x. Gas chromatography was applied to determine the concentration of the detonating cord's post-blasting gases, specifically hydrogen (H_2) and hydrocarbons – unsaturated: ethene (C_2H_4) and saturated: methane (CH_4) and ethane (C_2H_6).

2.2.2. Results

Average values for three determinations of CO, CO_2, NO, NO_2, and NO_x concentrations expressed in ppm, %V/V and also - in litres per kilogram of the detonating cord are presented in Table 3.

Table 3. Results of determination of CO, CO_2, NO, NO_2, and NO_x concentrations after detonation of the detonating cord

Average values after detonation of three detonating cord charges	**CO_2***	**CO***	**NO***	**NO_2***	**NO_x***
Concentration of gase [ppm]	781.198	319.568	3.975	1.501	5.475
Concentration of gase [%]	0.078	0.032	0.000	0.000	0.001
Volume of gase [L/kg]	**220.80**	**90.41**	**1.12**	**0.43**	**1.55**

** - extrapolation of concentration to time t = 0 min (detonation of detonating cord charge)*

It was noted that analysis of post-blasting gases showed that each of the charges of detonating cord underwent full detonation.
In Table 4, results of this analysis, of the gaseous detonation products of penthrite detonating cord expressed in ppm, %V/V and calculated in litres per kilogram (L/kg) of the cord are presented. Hydrogen, ethene (C_2H_4) and ethane(C_2H_6) were detected and their concentrations determined. The analysis did not confirm the presence of methane (CH_4).

Table 4. Results of determination of gaseous detonation products of detonating cord using gas chromatography

Average values after detonation of three detonating cord charges	**H_2****	**CH_4****	**C_2H_4****	**C_2H_6****
Concentration of gase [ppm]	642	-	105	11
Concentration of gase [%]	0.0642	-	0.01050	0.00109
Volumet of gase [L/kg]	**62.40**	**-**	**10.20**	**1.06**

*** - average value of determination for time t = 10 min after detonating cord initiation*

3. Discussion of results

In order to assess the scale of emission to atmosphere of post-blasting gases after detonation of penthrite detonating cord for rocks as well as of gases caused by decomposition of the pyrotechnic mixture, calculations were carried out on the scale of gas emission generated during splitting of identical blocks of virgin rock, *i.e.* granite in the Zimnik quarry and limestone in the Wola Morawicka quarry.

Firstly, consumption of detonating cord and ROCKSPLITTER™ during splitting of the blocks was determined (Table 5). Secondly, volumes of the gases generated during the burning of ROCKSPLITTER™ (Tables 1 and 2) as well as the volumes of post-blasting gases generated by the detonating cord (Tables 3 and 4), were calculated as were values of post-blasting gasemissions to atmosphere caused by splitting of identical blocks out of virgin rock (Table 6).

Table 5. Consumption of detonating cord and ROCKSPLITTER™ item during splitting of natural rock blocks [2]

Quarry *(type of rock)*	Volume of the block [m^3]	Consumption of detonating cord		Consumption of ROCKSPLITTER™ item [kg]
		[m]	[kg]	
Zimnik *(granite)*	65	195	**9.945**	**7.65**
Wola Morawicka *(dense limestone)*	118	354	**18.054**	**13.75**

Table 6. Post-blasting gas emissions to atmosphere during splitting of identical natural rock blocks

Gas	Zimnik (granite)			Wola Morawicka (dense limestone)		
	Cord (9.9 kg)	ROCK-SPLITTER (7.65 kg)	Ratio of volumes of post-blasting gases Cord / ROCKSPLITTER	Cord (18.5 kg)	ROCK-SPLITTER™ (13.75 kg)	Ratio of volumes of post-blasting gases Cord / ROCKSPLITTER
	Volume of post-blasting gases [L]			Volume of post-blasting gases [L]		
CO_2	2195.86	469.10	4.68	3986.32	843.15	4.73
CO	899.13	184.14	4.88	1632.26	330.96	4.93
NO	11.14	2.45	4.55	20.26	4.4	4.60
NO_2	4.28	0.46	9.30	7.76	0.83	9.35
NO_x	15.41	2.91	5.30	27.98	5.23	5.35
H_2	620.57	29.30	21.18	1126.57	52.66	21.39
C_2H_4	101.44	25.86	3.92	184.15	46.48	3.96
C_2H_6	10.54	0	-	19.14	0	-

4. Summary

The composition of gaseous combustion products from the gas generating pyrotechnic device ROCKSPLITTER™ was determined and compared with that of detonation products of the alternatively used, penthrite detonating cord for rocks. Tests were carried out for splitting of identical blocks from virgin rock.

The above mentioned tests compare the emission to the environment of such gases as: nitrogen oxides, carbon oxides, hydrogen as well as saturated and unsaturated hydrocarbons. The results allow the conclusion to be made that gasgenerating devices of the ROCKSPLITTER™ type, generate much lower volumes of these gases, compared with penthrite detonating cords for rocks, under the same conditions.

The advantage of applying specialistic devices such as ROCKSPLITTER™, containing gas generating mixtures suitable for rock cleaving as well as for demolition of buildings, is the lack of necessity of applying common explosives, which have a negative impact on the environment *e.g.*: trinitrotoluene, nitroester-base explosives, ammonites, gun powders, detonating cords.

The use of gasgenerating devices such as ROCKSPLITTER™ eliminates formation of microcracks and crevices

in the monolithic rock and in the blocks being split off. The reason is that the deflagration reactions of pyrotechnic mixtures results in lower pressures being applied.
ROCKSPLITTER™ type devices stand out for their simple construction and low manufacturing costs.

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Literature

[1] a) Directive 2013/29/EU of the European Parliament and of the Council of 12 June 2013 on harmonisation of the laws of the Member States relating to the available on the market of pyrotechnic articles. Official Journal of the European Union L 178/27 dated 28.6.2013.; b) Polish Act of 13 April 2016 on change the law about explosives for civil uses and some other acts (in Polish). Journal of Laws of 19 April 2016, item 544.
[2] CEBAR-DG Company. Internal Report Warsaw 2015.
[3] Wang Mengmeng, Du Zhiming, Xu Taiwen. 2014. Analysis and purification of the combustion gas of gas generant. *Procedia Engineering* 84 : 826-833.
[4] Davis S.J., Miodownik A.P., Watts J.F. 1995. *Degassing and surface analysis of gas atomized aluminium alloy powders.* Journal of Materials Science 30 (15) : 3811-3819.
[5] Volk F., Schedlbauer F. 1989. Detonation Products of Less Sensitive High Explosives Formed Under Different Pressures of Argon and in Vacuum. *Proc. of the 9thSymposium (International) on Detonation*, OCNR 113291-7, Portland, Oregon : 384-392.
[6] Chen J.K., Brill T.B. 1991. Kinetics and mechanism of nitrate ester polymers at high heating rates by SMATCH/FTIR spectroscopy. *Combust and Flame* 85 (3-4) : 479-488.
[7] Oyumi Y., Brill T.B. 1985. Thermal decomposition of energetic materials 5. High-rate, in situ, thermolysis of two nitrosamine derivatives of RDX by FTIR spectroscopy. *Combust. and Flame* 62 (3) : 233-241.
[8] Zawadzka-Małota Iwona. 2008. The influence of structure and composition of mining explosives on content of toxic components in blasting gases. (in Polish) PhD dissertation. Katowice: Główny Instytut Górnictwa.
[9] Zawadzka-Małota Iwona. 2015. Testing of mining explosives with regard to the content of carbon oxides and nitrogen oxides in their detonation products. *Journal of Sustainable Mining* 14 : 173-178.
[10] PN-EN 13631-16:2006P: Explosives for civil uses – High explosives – Part 16: Detection and measurement of toxic gases. (in Polish).

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