

Utilization of Pyrotechnic Mixtures in Block Deposit Mining Operations

Józef Pyra ^{1,*}, Andrzej Maranda ², Bogdan Florczak ² and Rostyslav Zrobok ³

¹ Faculty of Mining & Geoengineering, AGH University of Science and Technology, Mickiewicza 30, 30-059 Cracow, Poland

² Łukasiewicz Research Network—Institute of Industrial Organic Chemistry, 6 Annopol St., 03-236 Warsaw, Poland

³ CEBAR DG Sp. z o.o., Al. Jerozolimskie 81, 02-001 Warsaw, Poland;

Featured Application: The results of the presented research can form the basis for the development of pyrotechnic mixtures used in mining method and extraction of rock blocks.

Abstract: The article presents the results of estimates of thermodynamic parameters (oxygen balance, pressure, temperature, gaseous products produced in the reaction, specific energy, and the combustion heat) for 11 pyrotechnic mixtures and the final product—gas generator prototype (RSP), which can be used in mines for producing blocks. In addition, formal and legal considerations have been presented, as well as the results of gas generators in Polish mines. To compare the effects induced by using a detonating cord and a gas generator prototype, a test was carried out in granite quarries involving the measurement, at the same points, of vibration and the air blast. As a result of the tests, limitations and possibilities of using gas generators were indicated.

Keywords: gas generator prototype; pyrotechnic mixture; block-mining; blasting

1. Introduction

The primary stage of exploitation in order to obtain rock blocks is the proper detachment of a rock part from a massif. The rock block should be detached from the massif in such a way as not to damage its internal structure. This is achieved by reducing the propagation of micro-cracks, which would later hinder or even disable stone processing, and at the same time protect the entire deposit. This requires the use of different exploitation technologies, whose selection criteria are related to mining conditions and the geological structure of the deposit. It should also be noted that an important aspect of the selection of mining technology is the economic criterion, as well as maximizing the use of the block deposit, thanks to which the exploitation ensures maximum profitability. Thus, the selection of an unsuitable exploitation method may result in irreparable damage to the rock massif, which in turn is associated with serious financial losses [1].

Selecting the mining method and extraction of rock blocks depends on a number of factors, which may include [2–5]:

- Rock type, its structure, texture, mineralogical composition, physical and mechanical properties, etc.,
- deposit conditions: Block separability deposition and shape of the deposit, shoaling stratification, grid of horizontal and vertical cracks,
- environmental conditions,

- experience in applying various methods and availability of equipment and materials.

Many stone varieties, and the variability of geological deposit structure, require different types of devices, which are characterized by different operation methods and their parameters. In terms of mining technology, the extraction method is the most important, which, within its definition, also includes activities related to the splitting of monoliths into smaller blocks [1,6–14]. Accordingly, the methods of rock block extraction can be carried out manually with the use of all kinds of machines (e.g., diamond saws, hydraulic splitters, disc saws, torches, etc.), use of explosives (classic method, Finnish method), or other alternative methods (e.g., water jet cutting, use of ultra and infrasound).

Currently, different methods of rock block detachment are being sought, thanks to which the use of deposit resources will increase while reducing exploitation costs. One of the research directions in this field is the use of pyrotechnic mixtures. As a result of the combustion of a mixture, gasses are emitted, which form high pressure that acts on walls of the blasting hole. Increasing pressure causes a rise in tension along the line of the drilled holes, and the rock breaks. The artificially created crack plane detaches the block from the main rock mass, and additionally, gas pressure pushes the block away [15,16]. In the case of pressure drop, the pyrotechnic mixture will slowly burn, and no mechanical work is performed, which distinguishes this product from traditional blasting methods. Further on, the paper presents research results on the selection of an optimal mixture. The calculations were aimed at estimating the predicted (theoretical) values of the thermodynamic parameters: Oxygen balance, pressure, temperature, specific energy, the combustion heat, and the amount of gaseous products formed depending on the forecast composition of the pyrotechnic mixture. In the following parts, by discussion on how to deploy gas-generating devices in the detachment of rock blocks and shows the result of ground vibration and air blast.

2. Thermodynamic Parameters of Pyrotechnic Mixtures

Equilibrium thermodynamic constants can be calculated for constant pressure conditions and in conditions with constant volumes. Calculations use the ideal gas equation of state (EOS) and the virial gas equation, especially for high pressure in a calorimetric bomb or in firearms. By using the virial equation, one can calculate pressures close to the experimental values. Calculation of the combustion heat is particularly interesting, because experimental measurements using a calorimetric bomb are sometimes difficult due to high temperatures or the erosiveness of reaction products.

Using the ICT-Thermodynamic Code software [17], the following was calculated under a constant load volume ($V = 0.1 \text{ g/cm}^3$): Oxygen balance (BT), pressure (p), temperature (T), gaseous products produced in the reaction, specific energy (E_s) and the combustion heat (Q_{ex}). On the basis of earlier studies [18], a mixture of chlorate (V) of sodium and diesel oil was chosen. An estimation was made for mixtures containing different component content. The compositions of the tested gas-generating mixtures are summarized in Table 1, while Table 2 shows estimates and thermodynamic parameters. The subsequent drawings illustrate the relationship between detonation parameters and oxygen balance (Figure 1), as well as the content of diesel oil (Figure 2), chlorate (V), and sodium (Figure 3).

Table 1. Composition of tested gas-generating mixtures (Adapted from [15]).

Component	Content [%]										
	1	2	3	4	5	6	7	8	9	10	11
Chlorate(V) sodium	95	94	93	92	91	90	89	88	87	86	85
Diesel oil	5	6	7	8	9	10	11	12	13	14	15

Table 2. Results of thermodynamic parameter calculations for gas-generating tested mixtures (Adapted from [15]).

No. of Composition	BT [%]	P [Bar]	T [K]	Gaseous Products [mole/kg]	Es [J/g]	Qex [J/g]
1	26.00	311	1839	20.66	316	2646
2	22.18	369	2127	21.64	383	3093
3	18.37	430	2401	22.53	450	3539
4	14.55	494	2664	23.24	515	3986
5	10.73	557	2907	23.81	575	4432
6	6.91	614	3111	24.33	629	4879
7	3.09	664	3265	24.88	675	5325
8	-0.72	705	3357	25.53	713	5644
9	-4.54	731	3367	26.36	738	5418
10	-8.36	741	3286	27.37	748	5192
11	-12.18	739	3154	28.50	747	4968

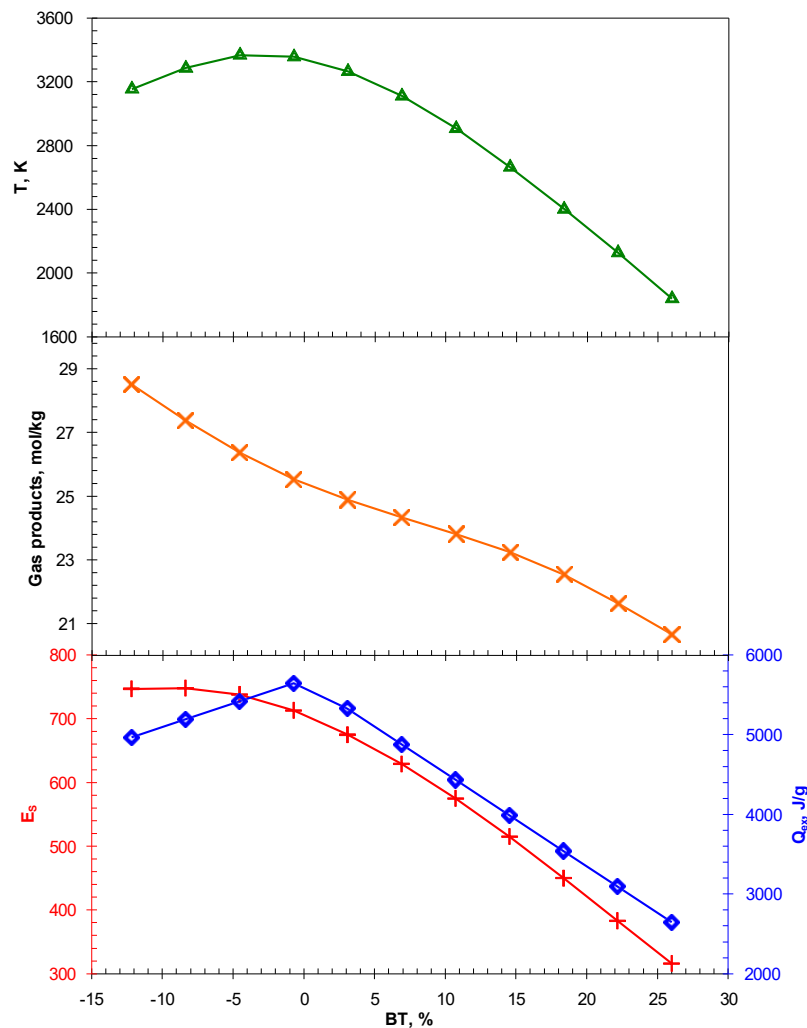


Figure 1. Relationship between thermodynamic parameters of tested mixtures and oxygen balance.

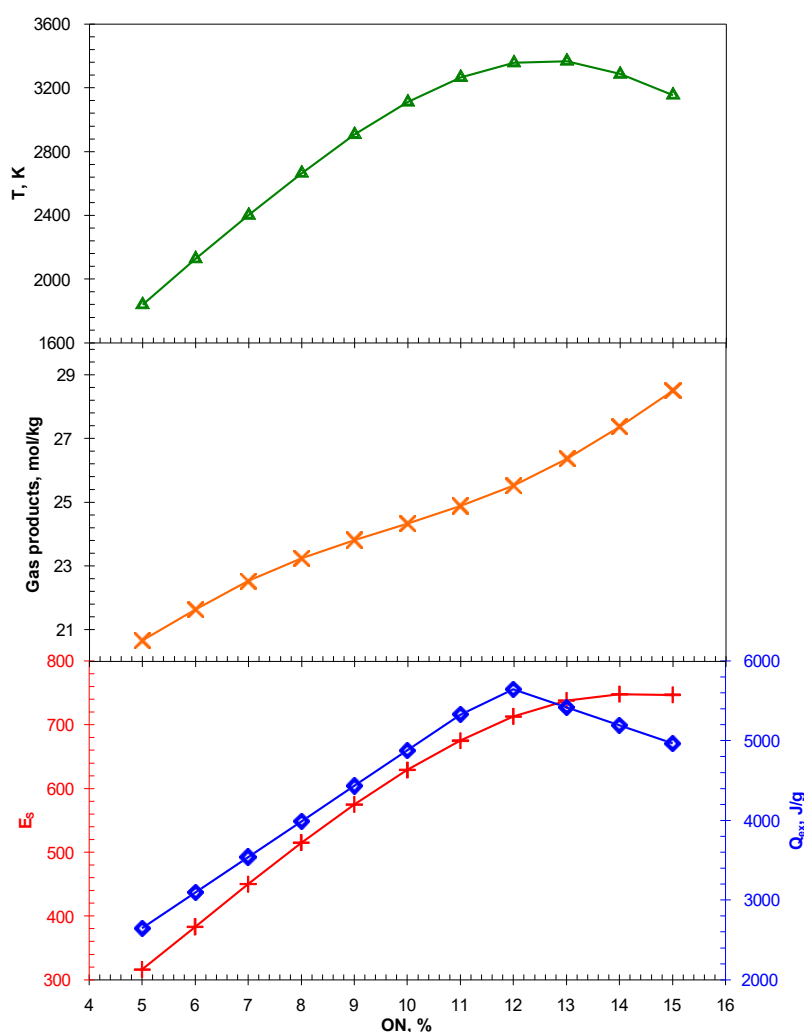


Figure 2. Relationship between thermodynamic parameters of tested mixtures and diesel oil content (ON).

From the data presented in Table 1, it can be concluded that thermodynamic parameters of the tested gas-generating mixtures are dependent on their composition in various ways, and hence on the content of components. Increasing the content of diesel oil causes a continuous lowering of the oxygen balance, and an increase in the volume and pressure of the gaseous combustion products and specific energy.

For the other established thermodynamic parameters, maximum values were obtained at different oil content. The maximum combustion temperature value was 3367 K (Table 2, composition 9) with a diesel oil content of 13%, and gross calorific value 5644 J/g (Table 2, composition 8), with oil content at 12%.

On the basis of the experimental test results and numerical estimates, an active mixture composition was selected, which was used in a gas generator prototype (RSP). The prototype was subjected to a full approval procedure, which resulted from the introduction of a new blasting method to be used in mines. The certificate from Notified Body No. 1453—Central Mining Institute, “Barbara” Experimental Mine—qualifies RSP as a P2 pyrotechnic article (other pyrotechnic products). However, according to opinions of the President of the State Mining Authority in Katowice, in mines, the product is classified as a blasting method, and its application requires that any procedures covering blasting activities be followed.

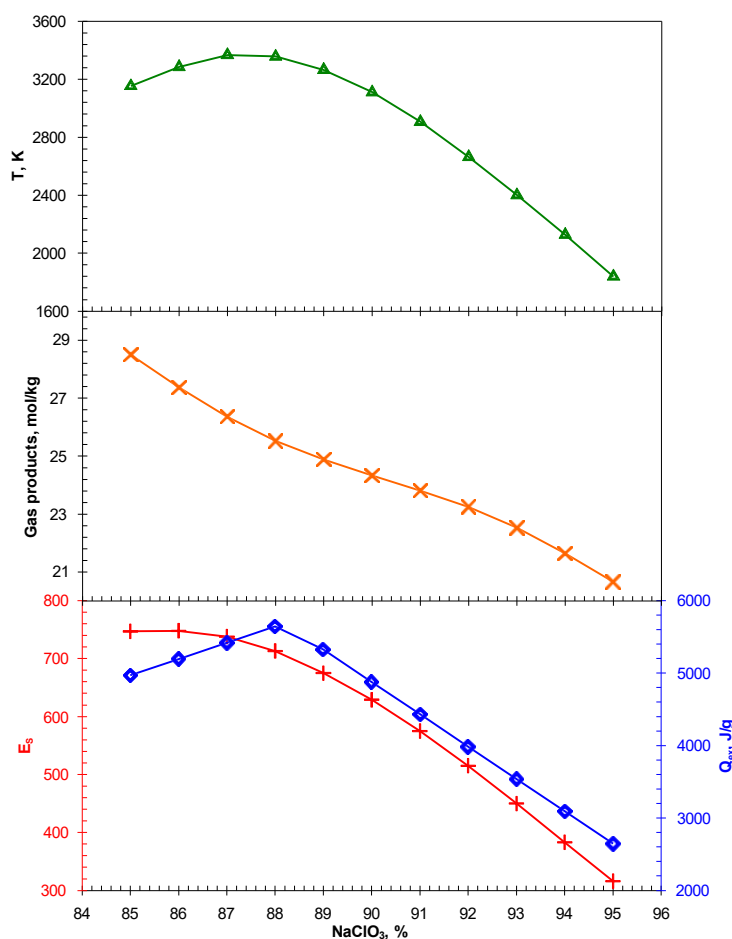


Figure 3. Relationship between thermodynamic parameters of tested mixtures and content of sodium chlorate (V).

3. Formal and Legal Aspects Concerning the Use of Pyrotechnic Mixtures

Gas generators developed and introduced on the Polish market are considered pyrotechnic products, and during the classification procedure referred to in Annex A to ADR agreements (European Agreement concerning the International Carriage of Dangerous Goods by Road), they were placed among Class 1 hazardous materials. As a consequence, according to the definition in Article 4 paragraph 1 point 1 in the Act of 21 June 2002, concerning explosives for civil uses [19], they are treated as explosives.

According to the definition contained in the provision in Article 6 point 14 of the Act of 9 June 2011, on Geological and Mining Law [20], explosives within the meaning of the Act of 21 June 2002, on explosives for civil uses, will be simultaneously classified as blasting products. As a result, the legal requirements referring to the use of gas generators in mining will be governed both by provisions of the law on explosives for civilian use, executive orders issued under this Act, and by the Geological and Mining Law, as well as executive orders issued thereupon.

Accordingly, to apply the RSP in mines, the same procedure is required as for the introduction of a new blasting method, the difference being that a permit is not required for transportation, as referred to in Article 2, paragraph 4.1 of the Journal of Laws of 2015. In accordance with this regulation, the requirements set forth in the explosives for civil uses Act concerning transport do not apply to pyrotechnic articles.

Chiefly, gas generators can be put to use in the mining industry in two manners. The first encompasses filing an application for the acquisition and use of gas generators in a mining plant, and obtaining the relevant decision of the Director of the District Mining Office in this area—as well as with

respect to any blasting method. The other manner involves the signing of a contract on comprehensive blasting services with a specialized entity that has a license to trade in explosives.

Experimental blasting does not necessitate changes in the mine operation schedule, so in this case the blasting may be carried out on the basis of a certificate or documentation concerning experimental blasting, accompanied by an opinion of an expert on mining operations. If the mine operation schedule has been approved under the provisions in force before 1 June 2012, then, along with an addendum to the schedule, a blasting certificate must be submitted, concerning the application of gas generators.

4. General Rules for the Application of Gas Generators in Mines

Based on the in-field tests carried out thus far in mines located in various geological conditions, and on mining and geological conditions, general rules concerning the design and application gas-generating equipment have been defined.

Gas generator prototype is intended for exploitation works, including loosening and shredding, rock detachment from massifs, monoliths, and block splitting. Conditions concerning insertion into holes apply only to dry holes between 28 mm and 105 mm in diameter. For holes with water content, it can only be used after the removal of water, and this requirement arose from the need to use wads of high quality, which cannot be used in holes filled with water. To use gas generator prototype for the extraction of aggregate material, the massif that is to be mined should have at least two vertical divisibility planes, and one horizontal.

In the plane in which a body of material will be mined, blasting holes are drilled at diameters of 65 mm and a maximum of 115 mm. The distance between adjacent holes should be 75–90 cm (Figure 4), and their number depends on the length of the massif to be mined.

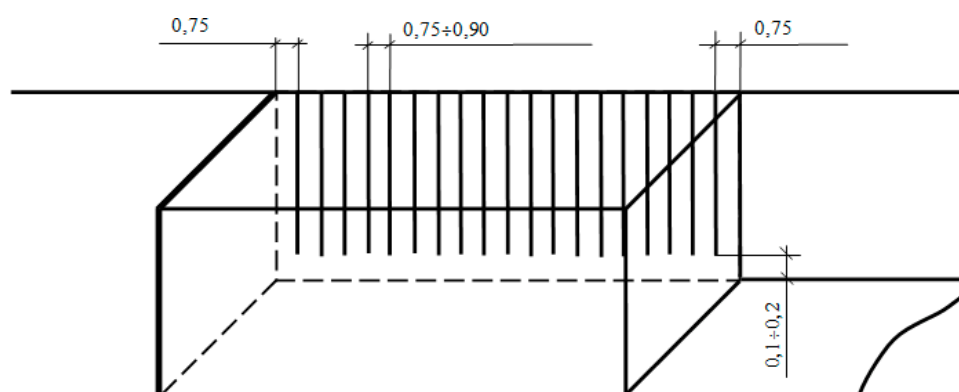
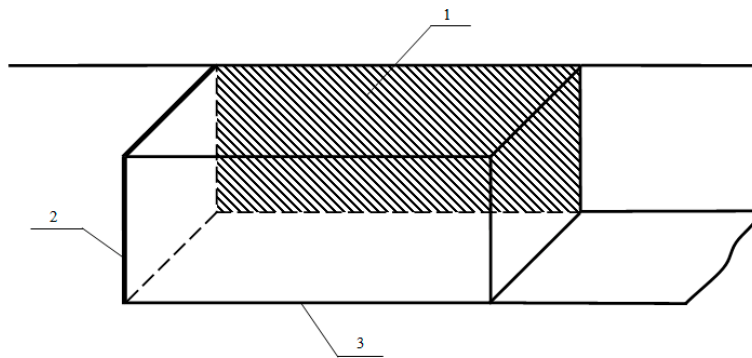


Figure 4. Diagram of hole spacing when mining aggregate material (Adapted from [16]).

To use gas generator prototype to extract stone blocks to obtain construction stone, the massif should have three outcropping planes (Figure 5).

In the plane on which the monolith is mined, blasting holes are drilled at a diameter of 28 mm and a maximum of 45 mm. The distance between the adjacent openings should be 25–30 cm. When the massif is characterized by a small number of natural layers and fractures, then the distance between adjacent holes may be 30–45 cm, while the distance between the extreme holes and the massif edge should be 10–15 cm. Hole spacing depends on the strength of the rock and the structure of the rock mass. Distance between holes drilled from the bottom of the horizontal slot (natural plane) should be 10–20 cm (Figure 6). The number of holes depends on the length of the mined block.



- 1 – division plane using ROCKSPLITTER,
 2 – vertical crack or gap obtained using a diamond saw or a thermo-cutter,
 3 – horizontal crack, natural footing or slot made using a diamond saw.

Figure 5. Massif prepared for mining blocks (Adapted from [16]).

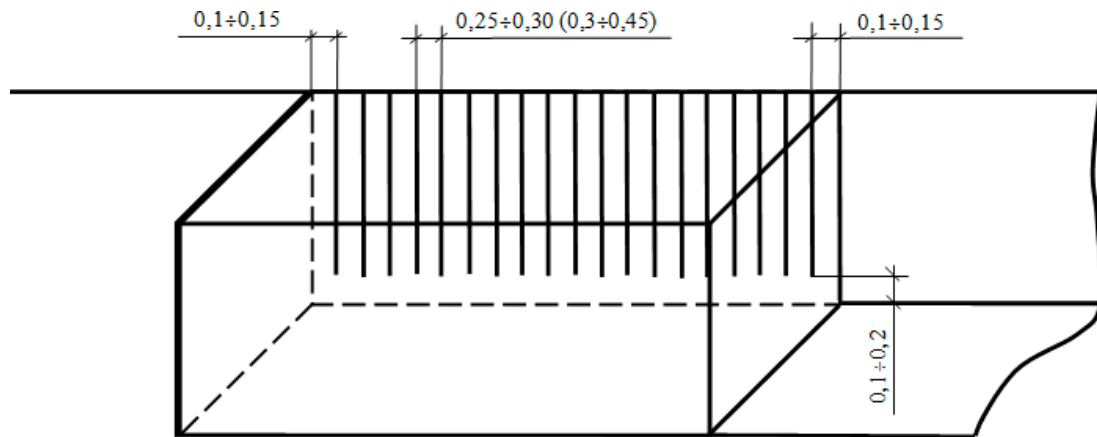


Figure 6. Diagram of hole spacing when mining blocks (Adapted from [16]).

Filling the holes and calculating the gas generator active mass should be carried out in the following proportions:

- For extracting aggregate: 150–200 g of pyrotechnic mixture per 1 m³ of the mined massif rock mass,
- for block mining: 60–120 g of pyrotechnic mixture per 1 m³ of rock mass of the mined block,
- for block detachment with three outcropping planes, one having been made with a diamond saw, with a small amount of cracks: 60–75 g pyrotechnic mixture per 1 m³ of rock mass of the mined block,
- for massif detachment, with three outcropping planes, and two of them (one horizontal and one vertical) are integrated and have a natural slot with a small amount of cracks: 80–100 g of pyrotechnic mixture per 1 m³ of rock mass of the mined block,
- for massif detachment, which has three outcropping planes, two of them (one horizontal and one vertical) are integrated and have a natural slot with a high amount of cracks: 100–140 g of a pyrotechnic mixture per 1 m³ of rock mass of the mined block.

5. The Results of Applying ROCKSPLITTER™ in Mine Conditions

In order to test the applicability of the gas generator prototype device in block mining, in-field tests were performed in a granite mine, where one blasting series was carried out. The diagram of the arrangement of RSP devices is shown in Figure 7, and the method of filling blast holes can be found in

Figure 8. In Figure 7, the colors show the weight of RSP applied (yellow — 100 g, red — 150 g). The total mass of pyrotechnic mixture used was 7650 g. Figure 9 shows the effect of blasting works, using RSP in a granite quarry.



Figure 7. Diagram of RSP arrangement when mining a block of granite.



Figure 8. RSP, and the method of its insertion into the blasting hole.

As shown in Figure 9, the pyrotechnic mixture enabled the mining of a rock block. Numerous cracks are clearly visible in the block, from the front and above. This is due to the fact that the tests were carried out in those parts of the deposit that were characterized by a very low ability to be blocked (due to the lack of certainty as to the proper effect of mining achieved with the tested gas-generating device). Moreover, unlike in block mining, which uses a detonating cord (DC), where DC fills the entire length of the blasting hole, in this case there is also the point arrangement of the gas-generating devices, which also results in non-uniform saturation of the rock with gases performing the mechanical work.



Figure 9. The effect of RSP in a granite deposit.

A similar attempt was also made in a limestone quarry. As in the granite quarry, a block of rock was detached and slightly pushed away from the body of material. Additionally, in this case, as a result of mining, the detached block broke. However, after transporting the block to work stations for further processing, there were no fracturing signs, which indicates that the cracks were formed along natural nonlinear portions of the body, and thus were immediately exposed.

In order to compare the effects induced by using a detonating cord and a gas-generating device, a test was carried out in granite quarries involving the measurement, at the same points, of vibration and the air blast (used Vibralock ABEM Instrument AB). For this purpose, along with a series using RSP, a rock block was prepared for mining using a detonating cord. Measurement stations were placed directly on the solid rock near the blasting sites with a detonation cord and RSP. At each station, there was also a ribbon microphone to measure the pressure of the air blast (marked M).

The use of a detonating cord to detach a block of rock was carried out in accordance with certificates prepared for exploitation purposes, as though it was performed in the everyday practice of the mine. The dimensions of the rock block detached with a detonating cord were as follows: Height—4.8 m, width—2.4 m and length—10 m. In total, 6.6 kg of detonating cord were used, at a weight of 20 g explosive per linear meter.

Examples of measurement results from position No. 1, at a distance of 13 m from the series are summarized in Table 3, where, in addition to measurement stations, the parameters of registered vibrations are quoted (PPV v_z , v_x , and v_y , and corresponding frequencies f_z , f_x , and f_y on individual components, and space vector v_{zxy}) and the air blast (overpressure value and the corresponding frequency).

Table 3. Results of calculations of thermodynamic parameters of the tested gas-generating mixtures.

Position	Record	Residue, [m]	PPV, [mm/s]			Frequency, [Hz]			Vector, [mm/s]	
			v_z	v_x	v_y	f_z	f_x	f_y	v_{zxy}	
DC										
No. 1	719.0072	15	115.1	38.4	116.1	35.0	43.2	34.6	167.6	
No. 1M	microphone	15	1547.0	Pa		95.1	Hz			
RSP										
No. 1	719.0076	13	8.7	11.2	16.9	37.3	122.0	33.3	18.1	
No. 1M	microphone	13	80.0	Pa		38.2	Hz			

For comparative purposes, seismograms are shown for vibrations on three components, and a record of changes in the air blast pressure for station No. 1 (Figure 10) are given.

Preliminary analysis of the seismographs shows that the interaction excited by mining using RSP is significantly smaller compared to mining using a detonation cord. In Figure 10, the record excited by using RSP (green) is small. This is due to the fact that the vibrations excited by the detonation cord (brown) are much larger, and using the same scale, the reference results in flattening of the signal

induced by RSP. In the case of air blast records, it is clear that the detonating cord raised more pressure and the RSP record is invisible.

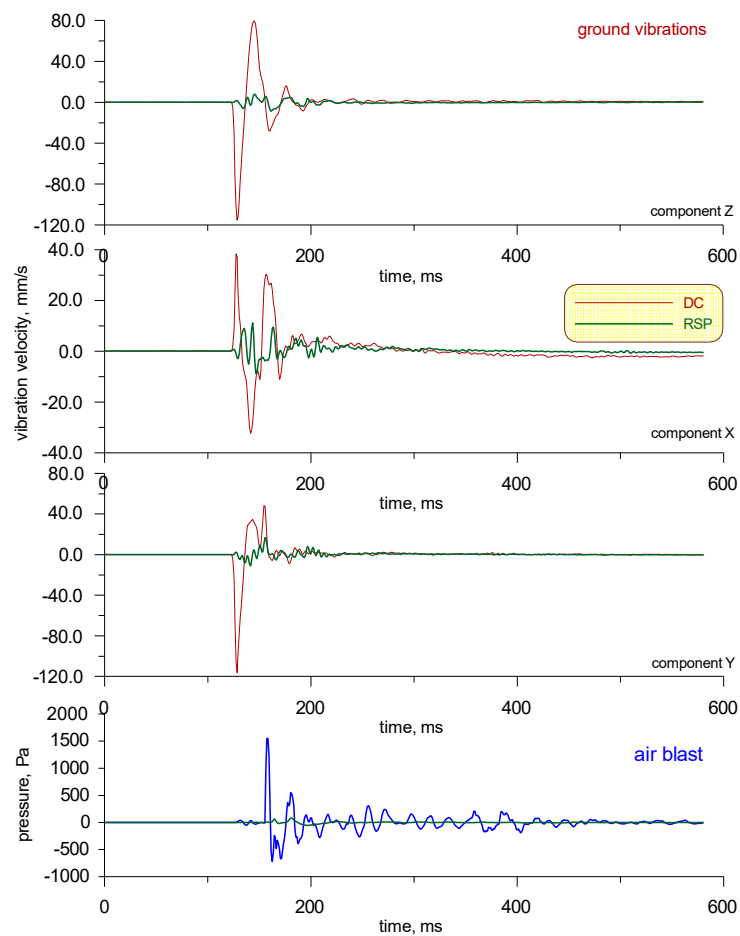


Figure 10. Comparison of vibration seismograms and PFU records at station of 1.

In order to better illustrate the difference, a division was made into individual components of frequency bands, with the use of third octave filters for the nearest station. Exemplary results from the horizontal x component and air blast pressure are shown in Figures 11 and 12, for stations 1 and M1.

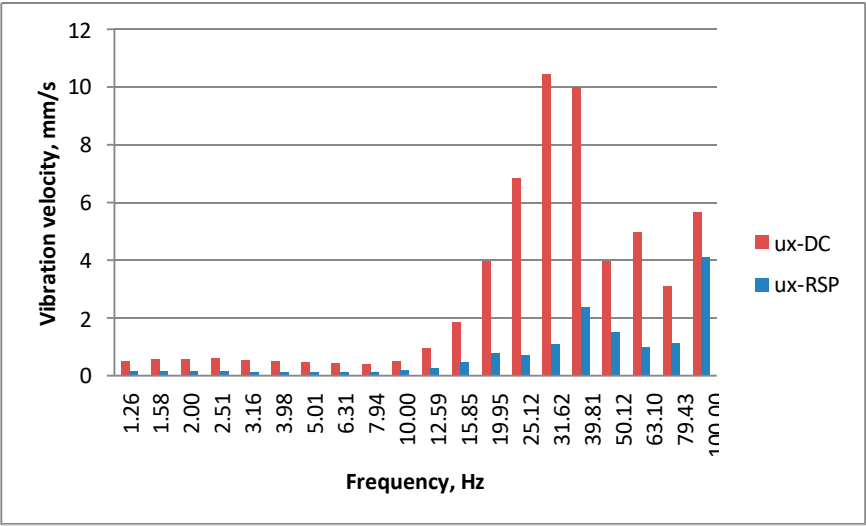


Figure 11. Result of the third octave analysis for the horizontal y component at station 1.

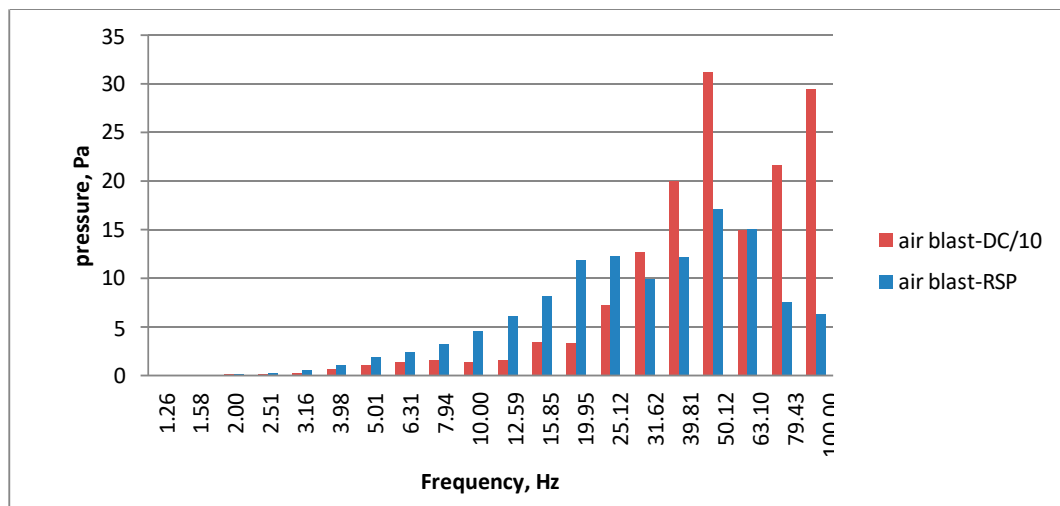


Figure 12. Result of the third octave analysis for air blast at station M1.

Analyzing Figure 11, one can see a clear difference in the intensity of vibrations induced by the primer cord detonation, and RSP-generated combustion. Vibrations induced using RSP, in individual third octave bands are much smaller. The distribution frequency is similar, but it is determined by the geological structure and immediate firing in both cases (no signal interference, which is usually caused by firing with a delay). The frequency structure of the air blast record may suggest a significant interaction of the acoustic wave (in order to better compare the air blast structure, the detonation cord values were divided by 12).

6. Discussion

The use of gas generators in extraction of rock blocks is an alternative method for those currently used. The use of an appropriate pyrotechnic mixture requires optimization of its thermodynamic parameters. In the next, they should be tested and allowed to be used in quarries. At the end, the distribution of gas-generating equipment should be adapted to local geological conditions.

Based on the results of preliminary experimental tests and numerical estimates, a composition of the pyrotechnic mixture was selected, which was used as the active element in the gas generator prototype. The product has undergone the entire procedure, which allowed its approval for use in Polish mines. It was found, inter alia, that in comparison with detonating cords, it generates fewer toxic products of high-energy transformation [21].

Preliminary studies carried out in mines showed that in comparison to detonating cords, RSP generates substrate vibrations of lower intensity, but has the same frequency structure, which is related to the geological structure of the deposit on which the measurements were made. In addition, when using RSP, no air blast is formed. The pressure changes recorded by microphones are actually associated with the occurrence of the acoustic wave, which is also smaller when RSP is used.

A key focus of the further work will be the refinement of the method of placement of equipment in blast holes, so that the concentration of energy could be as uniform as possible along the entire blasting hole, and not cause cracking of the mined rock blocks.

Author Contributions: Conceptualization, R.Z.; data curation, J.P. and B.F.; formal analysis, A.M.; methodology, J.P., B.F., and R.Z.; writing—original draft, J.P. and A.M.; writing—review & editing, J.P. and A.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kukiałka, S. Stone dressing and regular stone blocks mining—Selected problems. *Surf. Min.* **2006**, 3–4, 126–131. (In Polish)
2. Strykowski, M. (Ed.) *Innovative Technologies of Extraction and Processing of Block Rocks*; POIG–AGH–Poltegor: Krakow, Poland, 2012; ISBN 978-83-7783-044-4. (In Polish)
3. Kozioł, W.; Ciepliński, A. Dimension stone—Current tendencies in use, mining and processing, Pt. 1. *Mod. Build. Eng.* **2012**, 3, 76–77. (In Polish)
4. Kozioł, W.; Ciepliński, A. Dimension stone—Current tendencies in use, mining and processing, Pt. 2. *Mod. Build. Eng.* **2012**, 4, 82–85. (In Polish)
5. Kasztelewicz, Z. Extraction into blocks by blasting. *Krus. Prod. Transp. Zastos.* **2013**, 1, 44–47. (In Polish)
6. Mosch, S.; Nikolayew, D.; Ewiak, O.; Siegesmund, S. Optimized extraction of dimension stone blocks. *Environ. Earth Sci.* **2011**, 63, 1911–1924. [[CrossRef](#)]
7. Matti, H. *Rock Excavation Handbook*; Sandvik Tamrock Corp: Stockholm, Sweden, 1999.
8. Krasnovskii, A.A.; Mirenkov, V.E.; Shutov, V.A. Studies on fracture of rock blocks. *J. Min. Sci.* **2006**, 42, 105–112. [[CrossRef](#)]
9. Konya, C.J.; Walter, E.J. *Rock Blasting and Overbreak Control*; No. FHWA-HI-92-001; US: Federal Highway Administration: Washington, DC, USA, 1991.
10. Bhandari, S. *Engineering Rock Blasting Operations*; A.A. Balkema: Rotterdam, The Netherlands; Brookfield, WI, USA, 1997.
11. Kılıç, A.M.; Yasar, E.; Erdoğan, Y.; Ranjith, P.G. Influence of rock mass properties on blasting efficiency. *Sci. Res. Essays* **2009**, 4, 1213–1224.
12. Adebayo, B.; Umeh, E.C. Influence of Some rock properties on blasting performance: A case study. *J. Eng. Appl. Sci.* **2007**, 2, 41–44.
13. Onyelowe, K.C.; Bui Van, D.; Orji, F.; Nguyen Van, M.; Igboayaka, C.; Ugwuanyi, H. Exploring rock by blasting with gunpowder as explosive, aggregate production and quarry dust utilization for construction purposes. *Electron. J. Geotech. Eng.* **2018**, 23, 447–456.
14. Olofsson, S.O. *Applied Explosives Technology for Construction and Mining*, 2nd ed.; Applex: Arla, Sweden, 1990.
15. Maranda, A.; Florczak, B.; Gołańbek, B.; Korytkowski, B.; Pyra, J.; Ciosmak, H.; Zrobok, R. Rocksplitter—Gas expander to quarrying operations on the blocks and execution of specialized blasting works. *Surf. Min.* **2015**, 5, 49–56. (In Polish)
16. CEBAR-DG Sp z o. o. ROCKSPLITTER. *Pyrotechnic Article (Gas-Generating Device)*; Instructions for use of the product; CEBAR-DG Sp z o. o.: Warsaw, Poland, 2013. (In Polish)
17. Bathelt, H.; Volk, F.; Weindel, M. *The ICT-Thermodynamic Code (ICT-Code) Version 1.00*; User's Manual; Fraunhofer ICT: Pfinztal, Germany, 1988–2000.
18. Orzechowski, A.; Powała, D.; Sierżputowski, L.; Witkowski, W.; Maranda, A.; Zrobok, R. Studies on active mixtures for a Rocksplitter-type gasifier. *Chem. Ind.* **2016**, 95, 2461–2464. (In Polish)
19. ACT of 21 June 2002, Explosives for Civil Uses. *J. Laws* **2015**, 2015, 1100. (In Polish)
20. ACT of 9 June 2011, Geological and Mining Law. *J. Laws* **2014**, 2014, 613. (In Polish)
21. Zawadzka-Małota, I.; Zrobok, R. Investigations of gaseous combustion products of pyrotechnic gas generator “ROCKSPLITTER™”. *High Energetic Mater.* **2016**, 8, 27–32. (In Polish)