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Analytical paper / Praca analityczna

Selection of energy-optimal formulations for low detonation velocity explosive mixtures based on withdrawn explosives
Wybór optymalnych składów mieszanin wybuchowych o niskiej prędkości detonacji opartych o składniki pozyskane z wycofanych z użytku materiałów wybuchowych

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Abstract: *The article proposes the selection of components of explosive mixtures based on the recycling of withdrawn explosive materials with optimal explosive parameters which can be applied in demining, compacting soil masses for construction, or establishing temporary airstrips in open terrain. Their physicochemical and dynamic characteristics are presented, and thermodynamic calculations of the materials are performed.*

Streszczenie: *W artykule zaproponowano dobór składu mieszanin wybuchowych na bazie materiałów wybuchowych pochodzących z recyklingu, o optymalnych parametrach wybuchowych, które mogą znaleźć zastosowanie przy rozminowywaniu terenów zaminowanych, zagęszczaniu masywu gruntu pod budowę czy przy urządzaniu tymczasowych pasów startowych na lotniskach polowych. Podano ich właściwości fizykochemiczne, dynamiczne oraz obliczenia termodynamiczne badanych materiałów wybuchowych.*

Keywords: *explosive material, formulation, low-velocity explosive mixtures, gaseous detonation products, heat of explosion, detonation velocity*
Słowa kluczowe: *materiał wybuchowy, formulacja, mieszaniny wybuchowe o małej prędkości detonacji, gazowe produkty wybuchu, ciepło wybuchu, prędkość detonacji*

1. Introduction

Given the experience in using explosive energy for compacting structurally unstable, subsiding soils with different physical-mechanical characteristics, the development of new low-velocity explosive mixtures of low density to achieve the necessary uniform compaction over the required depth and the ability to control the seismic effect of the explosion, becomes relevant [1-3].

Controlling the impact on structurally unstable, subsiding soils through directed changes in explosive systems is of significant importance in geotechnology, mining operations, reclamation work, construction, and military matters. One solution to this problem is the selection and development of new explosive compositions depending on the tasks, physical-mechanical characteristics of the soils, and hydrogeological conditions of the proposed work.

2. Theory and investigated materials

When selecting formulations for the explosive compaction of structurally unstable, subsiding soils with different physical-mechanical characteristics, it is advisable to be guided by indicators which produce a longer effect on the soil mass and, at the same time, a gentler compression. This includes detonation velocity and critical diameter. Furthermore, global experience shows that the composition of explosives for soil compaction should have a low calorific value and a low volume of gas release during the explosion.

Based on the provided data and their analysis, compositions of mixed explosives and the percentage ratios of components were chosen for thermodynamic calculations. The main characteristics of hypothetical mixed explosive formulations based on potassium chlorate(VII) ($KClO_4$) with the addition of withdrawn explosive containing hexogen, as well as amatol, were investigated. Titanium dioxide (TiO_2) and barium nitrate(V) ($Ba(NO_3)_2$) were chosen as catalysts for the decomposition of $KClO_4$. Diesel fuel was added to the composition as an auxiliary fuel to improve organoleptic properties, reduce caking, and enhance combustion.

The paper presents the results of studies on the effectiveness of mixtures which include a component from one of the withdrawn explosives (Tables 1 and 2). When considering the characteristics of these explosives (Table 3):

- A-IX-1: 95% hexogen and 5% wax,
- A-IX-2: 75% hexogen, 23% aluminium (Al) and 2% wax,
- MS: 57% hexogen, 19% trinitrotoluene (TNT), 17% Al and 7% ceresin, and
- amatol: 60% hexogen and 40% TNT,

it can be seen that, despite their relatively small critical diameter, they have detonation velocities ranging from 4700 to over 5000 m/s. Therefore, the explosive components in their pure form, with such detonation velocities, are unsuitable for compacting a soil mass, for example, for softening the reflection of block stone, and so on. Since a drawback of these explosives is the large volumes of gas generated during detonation, including toxic gases, the selection of components took into account the environmental factor.

Table 1. Component composition of investigated mixed explosive formulations based on withdrawn explosives

Component name	Component content [%]										
	1	2	3	4	5	6	7	8	9	10	11
$KClO_4$	88.0	91.0	89.0	82.0	83.0	89.0	87.0	93.0	86.0	87.0	85.0
A-IX-1	–	–	5.0	8.0	10.0	–	–	–	–	–	–
A-IX-2	–	–	–	–	–	5.0	8.0	–	–	–	–
MS	–	–	–	–	–	–	–	5.0	8.0	–	–
Amatol	–	–	–	–	–	–	–	–	–	7.0	10.0
$Ba(NO_3)_2$	5.0	5.0	–	3.0	4.0	3.0	3.0	–	3.0	3.0	3.0
TiO_2	4.0	–	3.0	3.0	3.0	–	2.0	2.0	–	–	2.0
Diesel fuel	3.0	4.0	3.0	4.0	–	3.0	–	–	3.0	3.0	–

Table 2. Chemical composition of mixed explosive formulations based on withdrawn explosives

Component name	Component content [%]										
	1	2	3	4	5	6	7	8	9	10	11
$KClO_4$	88.0	91.0	89.0	82.0	83.0	89.0	87.0	93.0	86.0	87.0	85.0
Hexogen	–	–	4.75	7.6	9.5	3.8	6.1	2.9	4.6	–	–
TNT	–	–	–	–	–	–	–	0.9	1.5	1.4	2.0
Al	–	–	–	–	–	1.0	1.6	0.9	1.4	–	–
Ceresin	–	–	0.25	0.4	0.5	0.2	0.3	0.3	0.5	–	–
Ammonium nitrate(V)	–	–	–	–	–	–	–	–	–	5.6	8.0
$Ba(NO_3)_2$	5.0	5.0	–	3.0	4.0	3.0	3.0	–	3.0	3.0	3.0
TiO_2	4.0	–	3.0	3.0	3.0	–	2.0	2.0	–	–	2.0
Diesel fuel	3.0	4.0	3.0	4.0	–	3.0	–	–	3.0	3.0	–

Table 3. Characteristics of investigated conversion explosives

Characteristics	A-IX-1	A-IX-2	MS	Amatol
Critical diameter [mm]	20	20	15-20	40-50
Detonation velocity [m/s]	6000	5800	5400	4700

3. Analysis, results and discussion

For formulations from Table 2, thermodynamic calculations were performed using the Avakyan method, which allows for the theoretical determination of the following energetic and explosive characteristics of explosives: heat of explosion, temperature, volume of gases generated during explosion, oxygen balance, detonation pressure, detonation velocity, work capacity, and more [3, 4]. These calculations were conducted for preliminary energetic assessment (Table 4).

Table 4. Thermodynamic characteristics of explosive mixtures

Characteristic	Sample number										
	1	2	3	4	5	6	7	8	9	10	11
Oxygen balance [%]	31.8	29.7	28.2	23.2	36.1	28.5	37.3	41.8	25.2	30.7	40.3
Detonation heat [kJ/kg]	1027	1368	1795	2595	1821	2222	1751	1274	2612	1674	1035
Detonation temperature [K]	1295	1912	1970	3000	1230	2425	1580	1100	2738	2020	1857
Gas volume [dcm^3/kg]	313	319	335	600	314	319	307	314	340	350	346
Sensitivity [cm^3]	188	238	249	322	177	310	240	170	325	260	150
Critical diameter (experimental) [mm]	24	28	30	26	28	28	20	19	21	–	–
Detonation velocity (experimental) [m/s]	1920	1930	1970	1970	1950	1980	2810	2630	2770	–	–

From Table 4, it can be seen that all the samples have a positive oxygen balance, which is attributed to the relatively high content of $KClO_4$. Analysis of thermodynamic calculations allows us to conclude that the requirements for detonation velocity and energy characteristics can be satisfied by formulations based on $KClO_4$ with the addition of decomposition catalysts and fuel. However, such mixtures may have a high critical diameter and would require a significant impulse for initiation [5-8]. Therefore, incorporating withdrawn explosive like A-IX-1, A-IX-2, MS, or amatol into the composition of the explosive mixture can improve its initiation conditions by reducing the critical diameter.

The table also includes experimentally determined critical diameter values using the cone method with a 5° opening angle and detonation velocity values for 52 mm diameter charges. Summarizing these data,

it can be noted that for mixtures based on A-IX-1, the critical diameter (d_{cr}) varies within the range of 24 to 30 mm with a detonation velocity (*D*) of 1920 to 1970 m/s. For A-IX-2 based mixtures, d_{cr}= 26-28 mm, D = 1950-1980 m/s, and for MS - based mixtures, d_{cr} = 19-21 mm, D = 2630-2810 m/s.
Thus, experimentally measured results indicate the achievement of the research goal – obtaining low-velocity explosive mixtures which do not contain nitroesters, with an acceptable critical diameter which meets the requirements for blasting block stone using borehole charges or small-diameter borehole charges.
In order to determine the quantity of gas released during the detonation of the samples of the explosive formulations (No. 1-11), calculations were carried out using the multifunctional "Astra" program - "Modeling of chemical and phase equilibria at high temperatures." The "Astra" program is designed to determine the equilibrium characteristics, phase composition, and chemical composition of various systems. The program is based on a universal thermodynamic method for determining the equilibrium characteristics of heterogeneous systems, which is based on the fundamental principle of maximizing entropy. The program allows for calculations of the quantity and composition of the gaseous products formed during combustion (with an excess of oxidizer) using higher valences of elements and heterogeneous environments along the shock wave front. The results of the calculations are presented in Table 5.

Table 5. Quantity of product released during detonation of explosive mixtures

Product name	**Quantity of product [mole/kg]**										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
O_2	7.58	7.53	7.40	6.10	9.25	7.30	9.23	9.60	6.52	8.05	10.41
H_2	0.16	0.24	0.23	0.42	0.06	0.23	0.43	0.02	0.32	0.31	0.12
H_2O	0.52	0,91	0.87	1.37	0.32	0.88	0.90	0.09	1.08	1.54	0.83
CO	1.51	1.93	1.92	2.78	0.84	1.89	0.66	0.57	2.50	1.56	0.32
CO_2	0.60	0.89	0.87	1.12	0.51	0.88	0.37	0.30	1.04	0.98	0.29
N_2	0.10	0.10	0.50	0.97	1.22	0.46	0.78	0,30	0.65	0.71	1.00
NO	0.16	0.16	0.34	0.43	0.56	0.32	0.46	0.29	0.36	0.38	0.48
Cl	–	1.54	1.58	1.45	1.38	1.50	1.48	1.69	1.48	1.22	1.08
HCl	0.38	0.48	0.48	0.58	0.26	0.47	0.21	0.16	0.52	0.54	0.36
$KCl_{(s)}$	4,00	4.30	4.20	3.70	4.10	4.20	4.32	4.65	3.95	4.34	4.53
$BaO_{(s)}$	0.13	0.12	–	–	0.10	–	0.13	–	–	–	–
$TiO_{2(s)}$	0.46	–	0.35	–	–	–	–	–	–	–	–
Total gas product	15.6	18.2	18.74	18.92	18.6	17.66	18.97	17.67	18.42	19.63	19.42

According to thermodynamic calculations, of the investigated low-velocity explosive mixtures, the optimal formulations are those based on a mixture of withdrawn explosive and the oxidizer potassium chlorate(VII) with additives. Specifically, the composition could be: withdrawn explosive (A-IX-1 or A-IX-2) – 8-10%; $KClO_4$ – 83-88%; decomposition catalysts for $KClO_4$ – up to 6%.
The analysis of data in Table 5 shows that during the explosion of the explosive formulations, a significant amount of oxygen is released due to the positive oxygen balance of the explosives. Non-toxic gases produced during detonation include water vapour, carbon dioxide, hydrogen, and nitrogen, which are components of the atmosphere. In samples Nos. 5 and 7, the content of toxic carbon monoxide (CO) during detonation is no more than 1 mole/kg, which is achieved through the appropriate oxygen balance of the explosive. The gaseous products also contain a small amount of nitrogen oxide (NO) – up to 0.5 mole/kg.
As for the decomposition products of the oxidizer $KClO_4$, chlorine and a small amount of HCl are present in the gaseous product. Among the chlorine-containing decomposition products of the explosive, the majority are condensed or particulates of KCl salt. Additionally, traces of titanium and barium oxides are present among the condensed products.

Overall, the gas composition of the decomposition products corresponds to that of safety explosives, where one of the components is NaCl. Considering that the applied area involves the simultaneous detonation of a small amount of such explosive material (up to 100 kg), the environmental condition in the atmosphere after the explosion should be satisfactory.

4. Conclusions

- ♦ The thermodynamic calculations of the investigated explosives show that by varying the content of active components of withdrawn explosives, such as A-IX-1 and A-IX-2, and introducing an inert admixture and other technological additives into the oxidizer, it is possible to obtain explosive compositions which meet the requirements for compacting structurally unstable soils. These explosives can provide the necessary stability for temporary airstrips and create the required explosive impulse for neutralizing mines.
- ♦ Taking into account that programs for determining the thermodynamic parameters of explosive mixtures are based on certain assumptions, the final determination of the composition should be adjusted based on practical measurements of explosive characteristics such as detonation velocity, critical diameter, and the completeness of detonation under experimental conditions.

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