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Investigation of the Influence of Cooling Salts upon the Explosive Performance of Emulsion Explosives

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Abstract: Emulsion explosives modified by the addition of cooling salts have been investigated. Sodium chloride and ammonium chloride were added as cooling agents. The research was carried out to develop emulsion explosives that can be applied in the coal mining industry. The particular requirements for the considered explosives must ensure a low hazard degree when used in the presence of coal dust and/or methane.

Experimental determination of the detonation velocity confirmed that the satisfactory performance of the investigated emulsion explosives, modified by the addition of these cooling salts, was preserved. In all of the investigated samples, the detonation velocity was about 4500 m/s, with salt contents of about 10-15%. In order to explore the thermodynamic characteristics of the investigated explosives, the chemical composition as well as the state parameters of the detonation and explosion products were evaluated. In these analyses, the cooling additives were allowed to become involved in chemical reactions during the attainment of thermodynamic equilibrium in the reacting mixture. The results obtained show reciprocal relations between the partial loss of explosive performance (diminution in explosion energy and lowering of the amount of products in the gaseous phase) and the desired reduction in temperature of the explosion products.

Keywords: emulsion explosives, cooling salts, explosion temperature and energy

1 Introduction

In recent decades various kinds of emulsion explosives have become the dominant shot agents employed in the mining industry. The growing use and significance of emulsion explosives arises as a result of several of their beneficial properties [1, 2]. Emulsion explosives exhibit apparently low mechanical sensitivity. Being water-resistant, emulsion explosives can withstand unfavorable geological conditions. The physical structure of an emulsion enables the mass density as well as the detonation velocity and detonation pressure of emulsion explosives to be adjusted to suit the characteristics of the blasted rock. Due to their low sensitivity, the mechanization of borehole filling has become widely employed. Important eco-friendly aspects resulting from the low concentrations of toxic gases in the detonation products of emulsion explosives should also be noted. A constant growth in the bulk of the orders and the increasing share of emulsion explosives in the range of industrially used explosives has been observed in Poland in recent years [3]. Emulsion explosives are mainly employed in opencast and in metal ore mining. The investigations presented here are intended to extend the range of emulsion explosives in the coal mining industry, especially in the possible presence of coal dust or methane.

In this paper the results of an investigation of emulsion explosives modified by the addition of cooling salts, sodium chloride and ammonium chloride, are presented. As the base, two types of emulsion matrix were chosen. Emulsion mixtures sensitized with glass microballoons are considered. The detonation properties of explosives containing of 5-15 wt.% of inert salts were investigated experimentally.

To examine the effect of cooling salts on the detonation performance and explosion processes, evaluation of the chemical composition and state parameters of the explosion and detonation products was performed. The possible participation of the added salts in all of the chemical reactions occurring in the explosion products was assumed. The values of the detonation velocities obtained in these evaluations were quite close to those recorded experimentally. This confirms that the diminution degree of the salt grains used was sufficient to ensure the participation and influence of the inert additives on the explosion parameters of the emulsion explosives investigated. The influence of cooling salts on diminishing the explosion temperature is discussed.

2 Technological Characteristics and Experimental Data

In the experiments performed, emulsion explosives based on two types of matrix were investigated. The formulation of the matrixes is presented in Table 1.

Table 1. Chemical composition of the base matrixes of the explosives investigated

Components, [%]	Matrix	
	M-1	M-2
Ammonium nitrate(V)	72.5	67.7
Sodium nitrate(V)	8.1	7.9
Fuel oil	6.7	6.7
Water	12.7	17.7

Electron microscope pictures of the matrixes employed are presented in Figures 1 and 2.

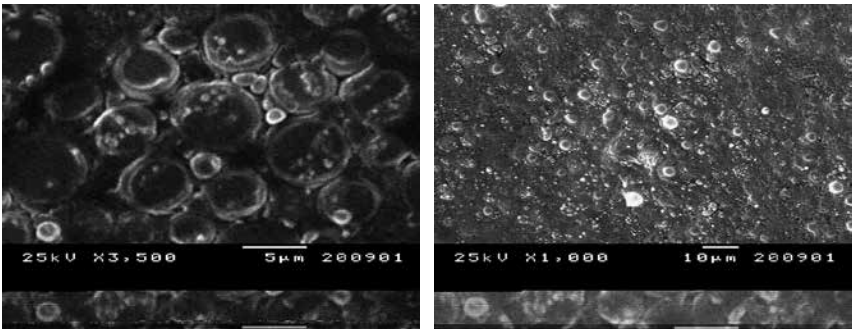

Figure 1. SEMs of matrix M-1.

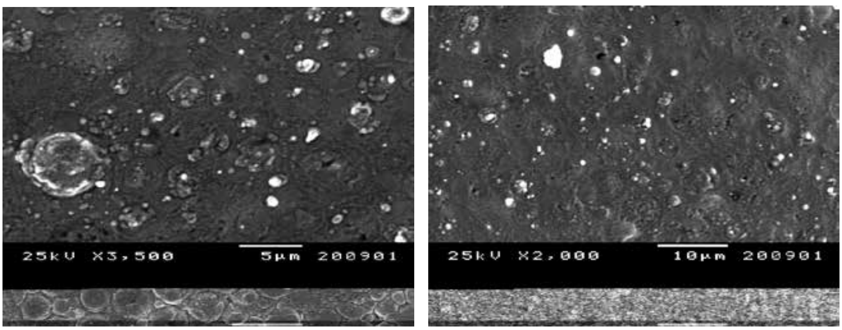

Figure 2. SEMs of matrix M-2.

The explosive mixtures were prepared by mechanical mixing of the constituents. In the first step the inert salts, sodium chloride or ammonium chloride, were added. Both salts had a similar range of grain diameters, 0.4-0.6 mm. The mixture was then sensitized by introducing glass microspheres (3%).

The glass microballoons were of type K1 of 3M Schotchlite production. The particle size distribution of the employed microspheres is presented in Figure 3 with electron microscope pictures of the microballoons in Figure 4.

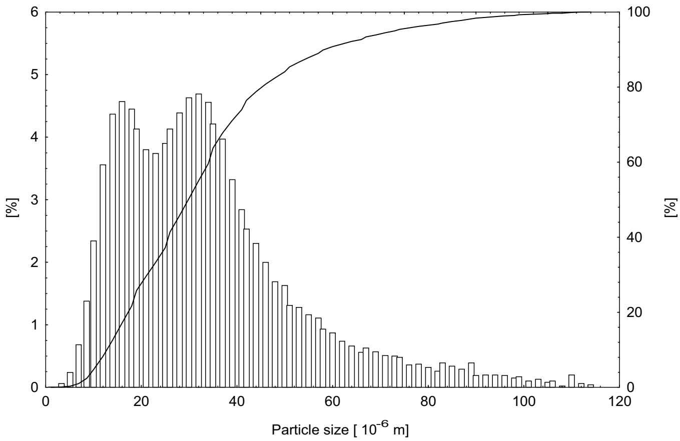

Figure 3. Particle size distribution of the glass microballoons.

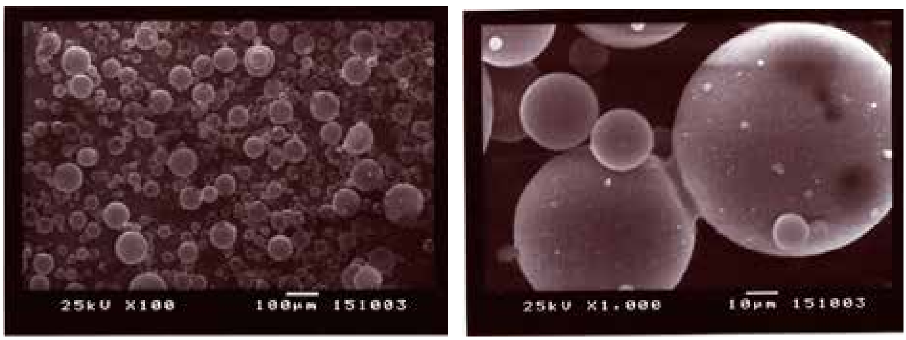

Figure 4. SEMs of the glass microballoons employed in the investigated explosives.

The detonation performance of the emulsion explosives obtained was tested by measurement of the detonation velocity. Test samples were assembled in 31/32 mm vinylidene tubes. The detonation velocities were registered by short-circuit gauges [3]. The results of the measurements of the detonation velocity of the investigated explosives are presented in Tables 2 and 3.

Table 2. Detonation velocities of the emulsion explosives based on matrix M-1

Explosive	1	2	3	4	5	6
Composition						
- matrix M-1	92	87	82	92	87	82
- glass microballoons	3	3	3	3	3	3
- sodium chloride	5	10	15	-	-	-
- ammonium chloride	-	-	-	5	10	15
Parameter						
- mass density, [g/cm^3]	1.18	1.19	1.21	1.16	1.16	1.16
- detonation velocity, [m/s]	4790	4670	4530	4830	4640	4470

Table 3. Detonation velocities of the emulsion explosives based on matrix M-2

Explosive	11	12	13	14	15	16
Composition						
- matrix M-2	92	87	82	92	87	82
- glass microballoons	3	3	3	3	3	3
- sodium chloride	5	10	15	-	-	-
- ammonium chloride	-	-	-	5	10	15
Parameter						
- mass density, [g/cm^3]	1.15	1.17	1.18	1.14	1.14	1.14
- detonation velocity, [m/s]	4680	4530	4460	4660	4420	4350

The developed explosives retained satisfactory detonation properties. In all of the investigated samples, the detonation velocity was about 4500 m/s, with salt contents of about 10-15%. To assess particular aspects of the presence of the inert salts and their effect on the explosion performance of the investigated explosives, an analysis of the chemical composition and thermodynamic parameters of the explosion products was carried out.

3 Thermodynamic Assessment of the Influence of Cooling Salts on the Temperature and Other Characteristics of the Detonation and Explosion of the Emulsion Explosives Considered

Thermodynamic evaluations were carried out to estimate the chemical compositions and state parameters of the explosion and detonation products. The MWEQ program [4] was applied. The program uses the principle of minimization of the free energy of the reacting mixture. The explosion products are considered as a reacting mixture for which the equilibrium point in multi-dimensional space of the species' concentrations is approached in an iterative way by the steepest descent method. The presence of substances in the condensed solid or liquid phases is accounted for. The implemented algorithm is based on a reduced set of equations that enables exact evaluation of the chemical substances that are present in the reactive mixture.

In the reacting medium that is generated in the explosion, the added salts behave in a several ways: to absorb the heat and remain in a condensed state, to vaporize or to undergo decomposition and react with other chemical substances that are present in the detonation/explosion products. In the evaluations performed, the added salts were assumed to participate in chemical reactions and to form equilibrium compositions of the transformation products.

The BKW [5] equation of state is used to describe non-ideal properties of chemical substances at high densities and temperatures. BKW is a semi empirical equation and several ways of adjusting the BKW parameter set have been proposed. In the evaluations performed, the BKWC parameterization [6] has been adopted. The BKWC set of parameters was developed by adjusting the evaluation results to data obtained from cylinder tests. In the optimization performed, BKWC covolumes of the main species present in the products of C-H-N-O-F-Cl explosives were derived [6]. In the explosives considered, sodium nitrate is introduced as the oxidizer in the M-1 and M-2 matrixes. To appraise the BKW covolumes of sodium containing compounds, the geometrical concept of Hobbes and Baer [7] was adopted. Values of the assumed BKW covolumes are presented in Table 4. The proximity of the van der Waal's radii of sodium and aluminum was taken as the basis for the assignment.

Table. 4. Geometrical assignment of BKW covolumes of sodium-containing chemical species

Species	Atom radius [Å]	BKW covolume*	Species	Atom radius [Å]	Assumed BKW covolume
Al	2.05		Na	2.31	
$Al_{(g)}$		340	$Na_{(g)}$		400
$Al_{2(g)}$		1400	$Na_{2(g)}$		1500
$AlH_{(g)}$		858	$NaH_{(g)}$		900
$Al_2O_{(g)}$		2130	$Na_2O_{(g)}$		2200
$AlOH_{(g)}$		884	$NaOH_{(g)}$		900
			$Na_2O_2H_{2(g)}$		2600

* Ref. [6]

As aluminum has three outer-shell electrons, while sodium has only one, a small difference in the assumed covolume values was assumed.

The results of the evaluation of the detonation and explosion parameters of the emulsion explosives based on the matrixes M-1 and M-2 are presented in Tables 5 and 6.

Table 5. Thermodynamic analysis of the transformation parameters of explosives based on the M-1 matrix

Explosive	Density [g/cm^3]	Transformation type	Q_v [MJ/kg]	p [MPa]	Σy_i [mol/kg]	T [K]	$y_{NaCl(s)}$ [mol/kg]	$y_{Na_2CO_3(s)}$ [mol/kg]
1	1.18	$D_{C\text{-}J}$ = 5102 m/s	2.735	7137	38.16	2206	0.8289	0.4517
		V = const	2.727	3320	39.92	1950	0.8416	0.4454
		p_{const}	2.260	0.101325	42.95	1573	-	-
2	1.19	$D_{C\text{-}J}$ = 4968 m/s	2.592	6674	37.62	2137	1.689	0.4256
		V = const	2.585	3106	37.72	1894	1.699	0.4204
		p_{const}	1.919	0.101325	41.61	1430	-	-
3	1.21	$D_{C\text{-}J}$ = 4863 m/s	2.451	6320	34.41	2063	2.548	0.3998
		V = const	2.445	2943	34.50	1833	2.557	0.3955
		p_{const}	1.598	0.101325	40.15	1285	-	-
4	1.16	$D_{C\text{-}J}$ = 5155 m/s	2.645	7229	41.97	2161	0.8768	-
		V = const	2.638	3361	42.07	1897	0.8767	
		p_{const}	2.298	0.101325	44.55	1556	-	-
5	1.16	$D_{C\text{-}J}$ = 5011 m/s	2.368	6776	41.78	2017	0.8291	-
		V = const	2.365	3148	41.85	1765	0.8291	-
		p_{const}	1.976	0.101325	44.96	1393	-	-
6	1.16	$D_{C\text{-}J}$ = 4856 m/s	2.092	6303	41.58	1870	0.7815	-
		V = const	2.093	2927	41.62	1630	0.7815	-
		p_{const}	1.795	0.101325	44.78	1282	0.6189	-

The detonation parameters at the C-J point were evaluated on the assumption of complete combustion of all of the ingredients comprising the initial explosive. The evaluated values of pressure (p), energy of explosion (Qv), temperature (T), as well as the amount of products in the gaseous phase (Sy_i) and the concentrations of species in condensed phases, sodium chloride and sodium carbonate, are

Table 6. Thermodynamic analysis of the transformation parameters of explosives based on the M-2 matrix

Explosive	Density [g/cm^3]	Transformation type	Q_v [MJ/kg]	p [MPa]	Sy_i [mol/kg]	T [K]	$y_{NaCl(s)}$ [mol/kg]	$y_{Na_2CO_3(s)}$ [mol/kg]
11	1.15	$D_{C\text{-}J}$ = 4856 m/s	2.456	6314	40.31	2031	0.8365	0.4371
		V = const	2.452	2940	40.39	1792	0.8459	0.4324
		p_{const}	1.955	0.101325	43.75	1394	-	-
12	1.17	$D_{C\text{-}J}$ = 4759 m/s	2.330	6014	30.07	1966	1.695	0.4122
		V = const	2.327	2801	30.14	1739	1.703	0.4083
		p_{const}	1.791	0.101325	41.64	1324	0.6406	-
13	1.18	$D_{C\text{-}J}$ = 4615 m/s	2.203	5576	35.85	1898	2.554	0.3875
		V = const	2.200	2599	35.91	1684	2.560	0.3843
		p_{const}	1.749	0.101325	38.97	1303	1.793	-
14	1.14	$D_{C\text{-}J}$ = 4941 m/s	2.372	6512	42.42	1989	0.845	-
		V = const	2.371	3028	42.48	1743	0.855	-
		p_{const}	1.996	0.101325	45.37	1303	-	-
15	1.14	$D_{C\text{-}J}$ = 4797 m/s	2.112	6084	42.20	1854	0.809	-
		V = const	2.114	2828	42.23	1619	0.807	-
		p_{const}	1.762	0.101325	45.394	1260	0.2906	-
16	1.14	$D_{C\text{-}J}$ = 4640 m/s	1.850	5634	41.99	1713	0.762	-
		V = const	1.854	2618	42.00	1489	0.762	-
		p_{const}	1.557	0.101325	45.40	1139	0.701	-

presented in Tables 5 and 6. Being of heterogeneous structure (Figures 1, 2, 4), the mixtures investigated exhibit non-ideal performance on detonation. The detonation velocities obtained in the evaluations are slightly higher than those obtained in the experimental determinations. The quite close agreement of the evaluated and the experimentally determined detonation velocities confirm that the method employed for the preparation of the explosive mixtures ensures an efficient course of the detonation process, and a predominant part of the explosive reacts in close proximity to the detonation zone.

By employing the explosive charge in a shot-hole, fast levelling of the thermodynamic parameters attained in the detonation zone occurs. In view of this, the explosion parameters at constant volume may be considered to be representative characteristics of explosives intended to be used in industrial applications. The cases indicated as V = const are evaluated at a constant volume, corresponding to the initial density of the mixture, $\upsilon = 1/\rho$ (given in the 2nd column).

Considering the possible use of the considered mixtures in a flammable atmosphere, the temperature of the expanded detonation products may also be of interest. The parameters attained on expansion to normal pressure of $p_{const} = 0.101325$ MPa, were then also estimated.

Except for a few cases of the detonation states, the temperature of the detonation and explosion products of the emulsion explosives considered do not exceed 2000 K.

4 Analysis of the Influence of the Cooling Salts on the Explosive Characteristics of Emulsion Explosives in a Broad Range of Salt Content

The results presented in Tables 5 and 6 illustrate the characteristics of a series of explosives for which experimental determination of the detonation velocity was performed (Tables 2 and 3). For a broader inspection of the influence of the cooling salts on the performance of emulsion explosives, a supplementary analysis of the dependence of the detonation and explosion parameters on cooling salt content has been carried out. The results of this analysis are presented in Figures 5 to 8.

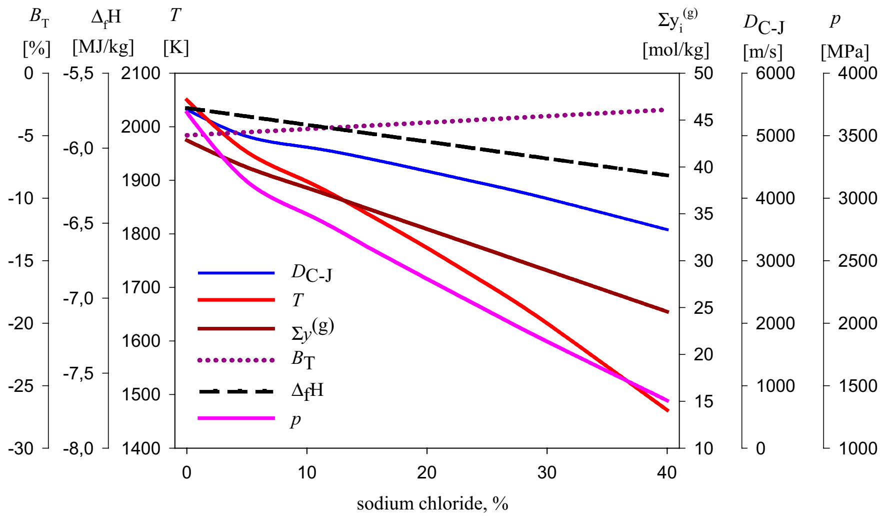

Figure 5. The dependence of the explosion parameters upon the sodium chloride content in emulsion explosives based on the matrix M-1.

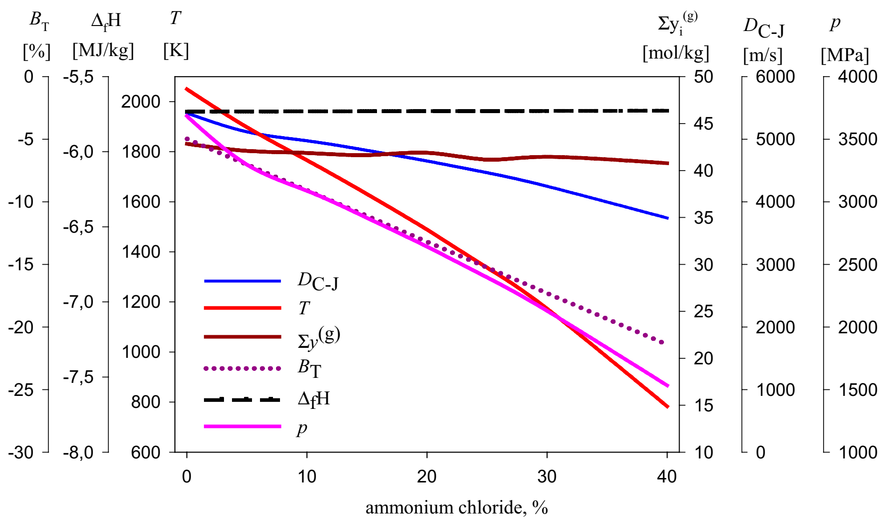

Figure 6. The dependence of the explosion parameters upon the ammonium chloride content in emulsion explosives based on the matrix M-1.

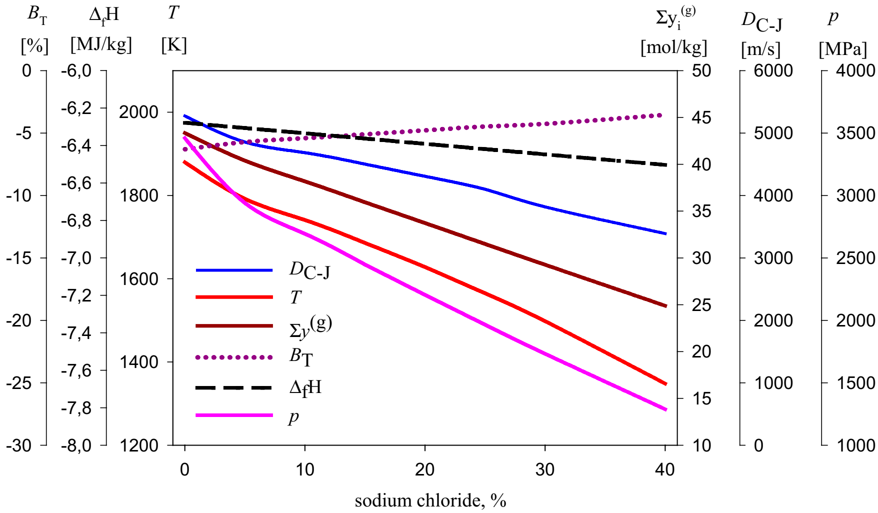

Figure 7. The dependence of the explosion parameters upon the sodium chloride content in emulsion explosives based on the matrix M-2.

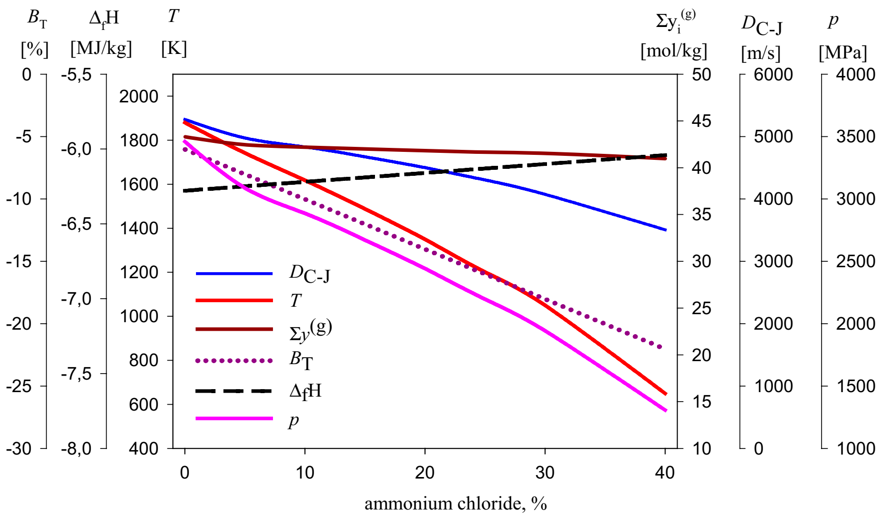

Figure 8. The dependence of the explosion parameters upon the ammonium chloride content in emulsion explosives based on the matrix M-2.

In Figures 5-8, values of the explosion parameters, explosion pressure and temperature p and T, and the amounts of products in the gaseous phase Sy_i, are presented. The evaluated values of the detonation velocity D_{C-J} are also shown.

To illustrate the initial characteristics of the considered explosives, values of the oxygen balance B_T and the enthalpy of formation D_fH are also shown. The addition of ammonium chloride leads to a significant lowering of the oxygen balance. That causes an increase in oxygen-lean chemical substances in the transformation products.

By employing a higher content of the cooling salts, a substantial decrease in the explosion temperatures may be attained. The evaluations performed indicate that with an ammonium chloride content over 30%, the explosion temperature may drop below 800 K. However, the reduction in temperature is accompanied by a considerable lowering of the explosion pressure, below 2000 MPa. That would limit the shattering effect of the explosive charges employed .

5 Conclusions

The energetic characteristics of emulsion explosives containing cooling salts, intended to be employed in the coal mining industry, were investigated. The role of sodium chloride and ammonium chloride as modifying additives was examined. The experimental determination of the detonation velocities confirmed that satisfactory performance of the explosive mixtures obtained on addition of the considered cooling salts was preserved. The determined detonation velocities were about 4500 m/s, with salt contents of 10-15%.

A thermodynamic analysis of the influence of the added salts upon the explosion temperature and energy, as well as on the amounts of gaseous products produced by the explosion of a unit mass of the energetic material, was performed. The dependence of pressure and temperature of the explosion products, as well the amounts of gaseous products per unit mass of explosive, was examined.

The reciprocal dependence between the positive influence of the added salts, that reveals, on the one hand, a lowering of the temperature of the explosion products, and on the other hand, a reduction in the explosive performance, is discussed.

6 References

[1] Mahadevan E.C., *Ammonium Nitrate Explosives for Civil Application*, Willey-VCH, Weinheim, **2013**, ISBN 978-3-527-33028-7.

[2] Wang X., *Emulsion Explosives*, Metallurgy Industry Press, Beijing, **1994**, ISBN 978-7502433819.

[3] Maranda A., *Industrial Explosives* (in Polish), Military University of Technology, Warsaw, **2010**, ISBN 978-83-61486-61-9.
[4] Papliński A., An Implementation of the Steepest Descent Method to Evaluation of Equilibrium Composition of Reactive Mixtures Containing Components in Condensed Phases, *Cent. Eur. J. Energ. Mater.*, **2006**, *4*(1-2), 135-150.
[5] Mader C.L., *Numerical Modeling of Explosives and Propellants*, CRC Press, Boca Raton, **1998**, ISBN 978-1-4200-5238-1.
[6] Fried L.E., Souers P.C., BKWC: An Empirical BKW Parameterization Based on Cylinder Test Data, *Propellants Explos. Pyrotech*., **1996**, *21*, 215-223.
[7] Hobbs M.L., Baer M.R., Nonideal Thermoequilibrium Calculations Using a Large Product Species Data Base, *Shock Waves*, **1992**, *2*, 177-187.