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Source / Izvornik: **Proceedings of the 25th Seminar on New Trends in Research of Energetic Materials, 2023, 461 - 469**

Conference paper / Rad u zborniku

Publication status / Verzija rada: **Published version / Objavljena verzija rada (izdavačev PDF)**

Permanent link / Trajna poveznica: https://urn.nsk.hr/urn:nbn:hr:169:138761

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Download date / Datum preuzimanja: **2024-07-31**

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Evaluation of input parameters for the non-ideal detonation model of emulsion explosives

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Abstract

Emulsion explosives exhibit non-ideal detonation behaviour. The degree of their nonideality depends mostly on their composition and density (i.e., porosity), which in turn is a function of amount of glass-microspheres added. Variation in composition results in a significant difference in the detonation properties. This presents an additional difficulty for numerical modelling of detonation of emulsion explosives since the input parameters for the modeling (such are reaction rate, equation of state of unreacted explosive, etc.) differ for each composition and density.

In this paper we present the results of calibration of the constants in pressure-dependent rate model incorporate in the Wood-Kirkwood detonation model. The constants are determined for several low-density emulsion explosives which contain up to 50% glass micro-balloons, in such a way that they reproduce the experimental detonation velocities-charge diameters data.

It was shown that pressure-dependent reaction rate model and the rate constants obtained in this study, can satisfactorily reproduce experimental detonation velocity-charge diameter for unconfined charges having densities in the range 0.5 to 1 g/cm^3.

Keywords: emulsion explosives; non-ideal detonation; Wood and Kirkwood theory; EXPLO5 code

1 Introduction

Emulsion explosives are mixtures composed of fine droplets of aqueous nitrate salts solution (oxidizer) separated by thin films of fuel and emulsifier and sensitized by glass micro-balloons (GMB) [1]. Thanks to their characteristics (such are low sensitivity, water resistance, and detonation properties) emulsion explosives are widely used in mining.

The detonation properties of emulsion explosives depend primarily on their composition (type and amount of aqueous nitrate salts used), density, and charge diameter, and may considerably vary (roughly from 2 to 6 km/s). On the other hand, the density is related the type and percentage of micro-balloons used as a sensitizer in an explosive mixture [2–4]. A lot of experimental research has been dedicated to finding relationship between detonation velocity, charge diameter, and density (i.e., porosity), and the main takeaway of this research is that detonation velocity increases with decrease of porosity until a maximum, after which it decreases [4,5] and that an increase in porosity results in decrease in the failure radius [2,3,6].

Detonation behaviour of emulsion explosives cannot be accurately modelled by the Chapman-Jouguet (CJ) and Zeldovich-von Neumann-Doering (ZND) detonation theories, i.e. they exhibit non-ideal behaviour. Such behaviour is manifested in strong dependence of detonation properties on charge diameter, existence and characteristics of confinement, a curved detonation front, a wide detonation reaction zone, and the presence of an unreacted fraction of

explosive at the sonic point [7,8]. The detonation theories that are capable to describe non-ideal behaviour of explosives must take into account the rate of radial expansion of detonation products in detonation driving zone and the rate of reaction. Some of such detonation theories are Wood-Kirkwood (WK) slightly divergent axial flow detonation theory [8,9] slightly divergent flow theory, or Detonation Shock Dynamics theory of Bdzil and Stewart [10].

The main difficulties related with practical application of these theories is the need to know the rate of chemical reaction and the rate of radial expansion of products. When it comes to emulsion explosives, additional difficulties are caused by the fact that properties of emulsion explosives significantly changes with porosity, which requires estimation of input parameters for numerical modelling for each composition and each porosity. It was shown by [11,12] that shock Hugoniot of unreacted explosive and detonation front curvature [12] change with the amount of glass micro-balloons. [13] reported that the rate constants in pressure-based and in Kirby and Chan's rate model [14] change also with porosity of emulsion explosives.

In this work we report on the applicability of pressure-based reaction rate model and Wood and Kirkwood detonation model to describe steady-state detonation of emulsion explosives with glass micro-balloons content up to 50%. The focus of the work is to estimate the rate constants as a function of glass micro-balloons amount.

2 Experiment and discussion

2.1. Description of detonation model

Detonation parameters of emulsion explosives, particularly detonation velocity, were calculated using the thermochemical code EXPLO5 and the Wood-Kirkwood detonation theory [15,16]. More information about the WK theory and its application in EXPLO5 can be found in [8,15,16]. In addition to detonation theory, EXPLO5 is supplemented by reaction rate, rate of radial expansion, and equation of state of detonation products and unreacted explosives.

The rate of reactions is described by single-step pressure-based reaction rate model [17,18]:

$$\frac{d\lambda}{dt} = k(1-\lambda)\cdot P^n \tag{1}$$

where λ is reacted fraction of explosive (conversion), and k and n are rate constants.

WK radial expansion model (ω_r) of detonation products is usually relate to the shock front curvature radius (Rc) calculated by dependence of R_C to failure radius (R_f), charge radius (R_0), and constants (a, b, and c) [19]:

$$R_C = aR_f^b R_0^c \tag{2}$$

Set of constants a = 4.7 , b = -0.6, and c = 1.37, determined in [19], have been found to satisfactory described the experimentally measured R_C for a series of emulsion explosives.

The state of gaseous detonation products is described by Becker-Kistiakowsky-Wilson EOS [15,20] and condensed detonation products by Murnaghan EOS [17,21]. Parameters in both EOSs are taken from EXPLO5 library [15]. Murnaghan EOS is given as [22]:

$$p = \frac{1}{\kappa m}\left[\left(\frac{V_0}{V}\right)^m - 1\right] \tag{3}$$

where V_0 is the molar volume of explosive when p = 0, κ is the inverse of the bulk modulus and m is the pressure derivative of the bulk modulus. The parameters m and κ can estimated using experimental shock Hugoniots data for emulsion explosives of varying densities and containing different amounts of GMB [23–26] and are calculated as: $m = (4s\text{-}1)$, and $\kappa = 1/\rho_0 C_0^2$ [22,27], where C_0 and s are constants from the shock Hugoniot equation given in the form $U=C_0+s\cdot u_p$. [13] found a roughly linear dependence of constants C_0 and s and the density of emulsion explosives:

$$C_0 = 2.103\rho_0 - 0.7787 \quad (4)$$
$$s = 0.7411\rho_0 - 0.6833 \quad (5)$$

2.2. Materials

For the analysis we used experimental data of [28,29].The authors used emulsion matrix of the following composition: 67% ammonium nitrate (AN), 14% sodium nitrate (SN), 12% water, 3% solid paraffin, 2% sorbitan monooleate, and 2% industrial oil. The density of the emulsion matrix (EM) was 1.41 g/cm^3. Hollow glass micro-balloons (having mean size of 58 μm, and the bulk density of 0.14–0.15 g/cm^3) were mixed to the emulsion matrix. The percentage of GMB (μ) in emulsion explosives varied from 4% to 50 % (over the mass of the explosive, μ=100(m_{GMB}/m_{EM}), which resulted in densities of explosives ranging from 1.1 to 0.51 g/cm^3. The failure radii of so obtained emulsion explosives varied between 2 mm (for μ=8%) and 5.6 mm (for μ=50 %), Table 1.

Table 1. Composition, densities, experimental detonation velocities of studied emulsion explosives [28]

Denotation	Percentage of GMB, μ (%)	Density, ρ_0 (g/cm^3)	Failure radius, R_f (mm)	D (d=20 mm), (km/s)	D ($d\rightarrow\infty$) (km/s)
EM	0	1.41			5.74[a)]
LDEM 5	5	1.12	3.7	4.60	5.53
LDEM 8	8	1.00	2.0	4.30	4.8
LDEM 15	15	0.84	2.5	3.50	3.75
LDEM 35	35	0.62	3.5	2.50	2.6
LDEM 50	50	0.51	5.6	1.94	2.19

Legend: a) D is detonation velocity, d is charge diameter, R_f is mean value of failure radius derived based on [28]

Experimental detonation velocities of studied emulsion explosives, as a function of inverse charge radii, are shown in Figure1.

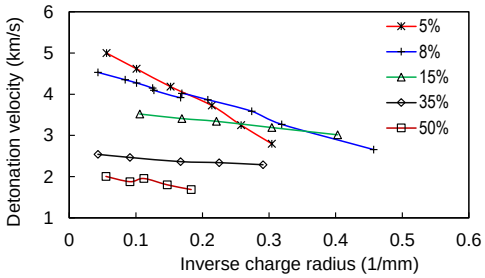

Figure 1. Dependence of detonation velocities on inverse charge radii for emulsion explosives containing different amounts of GMB (note: experimental data are taken from [28])

2.3. Calculation of ideal detonation velocities

Ideal detonation properties of studied emulsion explosives are calculated by EXPLO5 thermochemical code, applying the Chapman-Jouguet detonation model. The calculated detonation velocities (Table 2) are compared with the experimental detonation velocities (given in Table 1) for explosive charges having 20 mm diameter and with the detonation velocities at the infinite charge diameters (derived by extrapolation of experimental detonation velocity-charge diameter data) (Figure 2).

Table 2. Calculated ideal detonation properties of studied emulsion explosives

Composition of explosive				Calculation results				
Denotation of explosive	Percentage of GMB (over mas of matrix), (%)[a)]	Percentage of GMB in explosive (%)[b)]	Percentage of matrix in explosive (%)	D (km/s)	p_{CJ} (GPa)	T_{CJ} (K)	Q_{CJ} (kJ/kg)	V_0 at STP (L/kg)
EM	0	000	100.00	6.77	14.64	2247	3046	989
LDEM 5	5.00	4.76	95.24	5.35	7.73	2259	2879	952
LDEM 8	8.00	7.41	92.59	4.76	5.62	2243	2797	928
LDEM 15	15.00	13.04	86.96	3.96	3.45	2191	2627	873
LDEM 25	25.00	20.00	80.00	3.22	2.02	2107	2418	804
LDEM 35	35.00	25.93	74.07	2.81	1.42	2016	2239	745
LDEM 50	50.00	33.33	66.67	2.29	0.83	1893	2017	670

Legend: a) Percentage of GMB (over mas of matrix) is calculated by equation: μ=100(m_{GMB}/m_{EM}), b) percentage of GMB in emulsion explosive is calculated by equation: μ_{mix}=100(m_{GMB}/($m_{EM+}m_{GMB}$)), p_{CJ}, T_{CJ}, Q_{CJ}, and V_0 are detonation pressure, temperature, heat of detonation, and volume of gaseous detonation products at standard pressure and temperature respectively

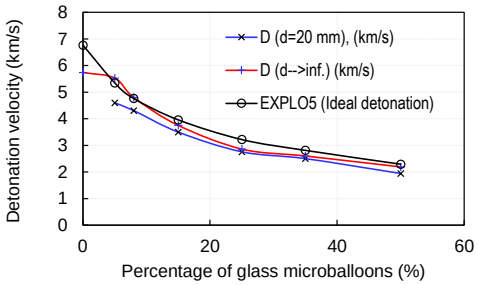

Figure 2. Comparison of calculated ideal detonation velocity and experimental detonation velocities for 20 mm charge diameter and for infinite charge diameter [28]

Figure 2 shows that calculated ideal detonation velocity agree very vell with the experimental detonation velocity at $d \rightarrow \infty$ (difference below 0.21 km/s). As expected, experimental detonation velocities for d=20 mm are significantly lower than ideal detonation velocity (for 0.35-0.75 km/s), which confirms the statement that the Chapman-Jouguet model cannot describe satisfactorily detonation behaviour of non-ideal explosives (it always overestimates detonation velocity). Lower detonation velocities for smaller charge radii are related to non-ideal behaviour of emulsion explosives, i.e., larger radial expansion of products and greater energy losses for smaller diameters.

2.4. Effect of GMB content and charge diameter on detonation velocity

Effect of charge diameter on detonation velocity for the studied emulsion composition having different content of GMB is modeled by Wood-Kirkwood detonation model incorporated in EXPLO5, as described in the section 2.1. The state of unreacted emulsion explosive is described by Murnaghan EOS (Eq.1), radial velocity is calculated by Wood-Kirkwood model (Eq.4), and rate of chemical reactions is calculated by pressure-based rate model (Eq. 6.). The constants in Murnaghan EOS and in radial expansion model are taken from our previous research [13,19] while the constants in reaction rate model are calibrated using experimental detonation velocity charge radius data.

The calibration of reaction rate constants k and n is relatively straightforward, and it is done for each emulsion explosive, i.e. each composition, as follows. For fixed value of constant n, constant k is varied so to best reproduce experimental detonation velocity inverse charge radius

data and experimental failure radius. As illustrated in Figure 3, the calculated failure radius can be increased by increasing n and decreasing k, while detonation velocity for the same charge radius can be increase by increasing k (Figure 3b). It was found that for $n > 1.3$, detonation velocity-inverse charge radius curve displays a turning-point behaviour in the steady detonation solution as the charge radius is decreased, which means that two steady detonation velocities are possible for the same charge radius. Similar behaviour is observed for ANFO explosives [14,18]. It should be mentioned that an additional criterion for calibration of the reaction rate model and the rate constants can be the width of detonation driving zone if such data are available.

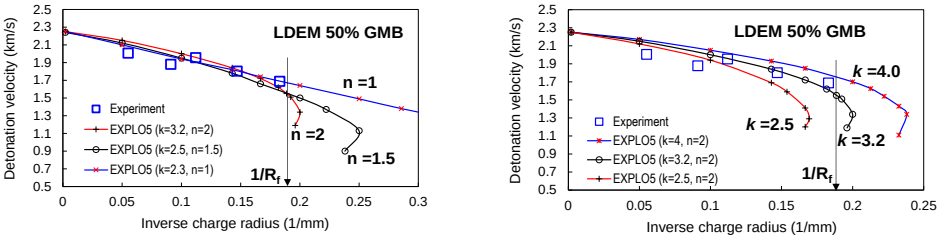

Figure 3. Effect of reaction rate constants k and n on detonation velocity-inverse charge radius curve profile

The values of the reaction rate constants derived in this way are given in Table 3. Along with the rate constants for [28] low-density emulsion explosives, the rate constants for ammonium nitrate/sodium nitrate-based emulsion explosive E-682 [23], which contains a smaller amount of GMB, are also given.

Table 3. Values of reaction rate constants for emulsion explosives containing different GMB amounts

Denotation of explosive	Percentage of GMS (%)	ρ_0 (g/cm^3)	Reaction rate constants (Eq.6)	
			k (1/μs)	n
E-682[a)]	3.28	1.17	0.061	2
LDEM 5	5	1.12	0.16	1.6
LDEM 8	8	0.99	0.38	1.5
LDEM 15	15	0.84	0.64	2
LDEM 15	35	0.62	2.2	2
LDEM 50	50	0.51	3.2	2

Legend: a) ammonium nitrate and sodium nitrate-based emulsion explosive E-682 [23]

Comparison of calculated and experimental detonation velocity-inverse charge radius profiles for the studied explosives is shown in Figure 4. It follows from Figure 4 that the calculation quite well describes experimental detonation velocity-inverse charge radii data for all studied explosives. As shown in Table 4, the difference between experimental and calculated detonation velocities at infinite charge diameter ($d \rightarrow \infty$) ranges between -0.27 and 0.16 km/s (i.e. below 6%). It can be also noted that the agreement between the experimental and calculated detonation velocities is quite good in the vicinity of the failure radius as well, where the Wood-Kirkwood detonation theory is less valid. In addition, the calculation reproduces accurately the failure radii (difference is below 0.5 mm).

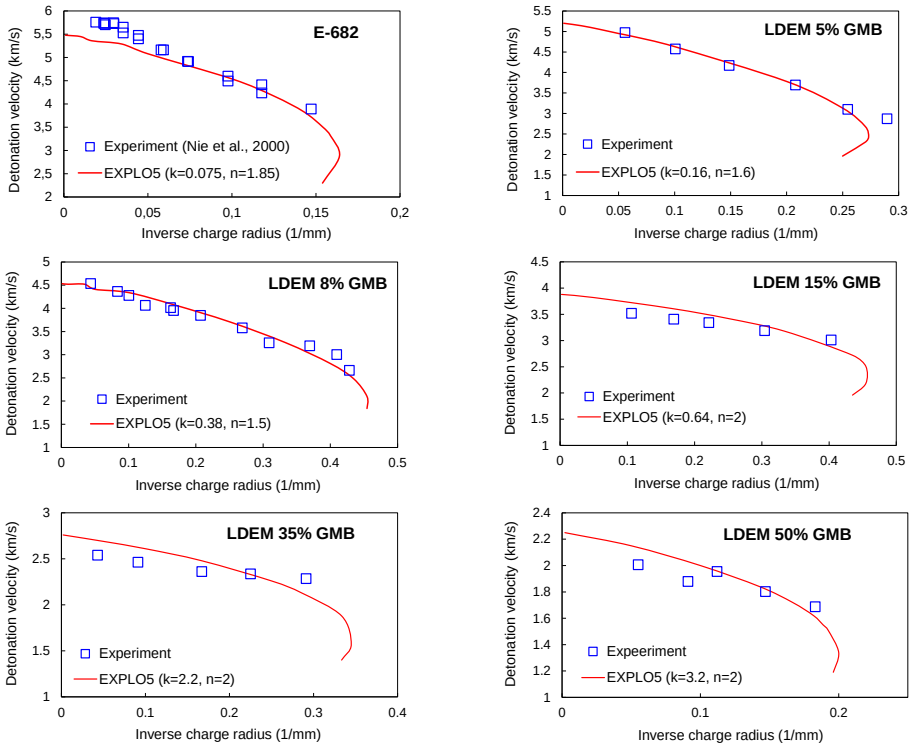

Figure 4. Comparison of calculated and experimental detonation velocities-inverse charge radii for emulsion explosives having different content of GMB

The drop in calculated detonation velocities in the vicinity of the failure radii, compared to ideal detonation velocity, ranges from about 34% (for μ > 15%) to about 54% (for μ<15%), which agrees with [28] experimental results.

Table 4. Comparison between experimental end calculated failure radii and detonation velocities at infinite diameter

Denotation	ρ_0 (g/cm^3)	Experimental		Calculated	
		R_f (mm)	D ($d\to\infty$) (km/s)	R_f (mm)	D ($d\to\infty$) (km/s)
E-682	1.17	6.2	5.77	6.1 (-0.1)	5.51 (-0.26)
LDEM 5	1.12	3.6	5.53	3.7 (+0.1)	5.20 (-0.33)
LDEM 8	1.00	2.0	4.80	2.5 (+0.5)	4.53 (-0.27)
LDEM 15	0.84	2.6	3.75	2.2 (-0.4)	3.89 (+0.14)
LDEM 15	0.62	3.5	2.60	2.9 (-0.6)	2.76 (+0.16)
LDEM 50	0.51	5.4	2.19	5.0 (-0.4)	2.24 (+0.05)

Legend: The difference between experiment and calculation is given in parentheses

It is obvious from Table 4 that the reaction rate the constant k significantly changes with density of explosive, i.e. with content of GMB, while the constant n varies between 1.5 and 2. For illustration, for LDEM5 5 k=0.16 1/μs and n=1.6, while for LDEM 50 k=3.2 1/μs and n=2, which means that k is increased by 20 times. This in turn indicates that, for the same conversion, pressure and n, reaction rate in the case of LDEM 50 is around 20 times higher than in the case of LDEM 5. Such result is consistent with the fact that GMB act as a sensitiser, i.e., as the hot-spots – higher GMB content, the faster the reactions in the early decomposition stage of emulsion

explosive. Figure 5a illustrates that the constant *k* (and rate of reactions) increases almost linearly with increase of GMB content, while Figure 5b shows that the constant *k* decreases roughly with the cube of density (i.e., increases with porosity).

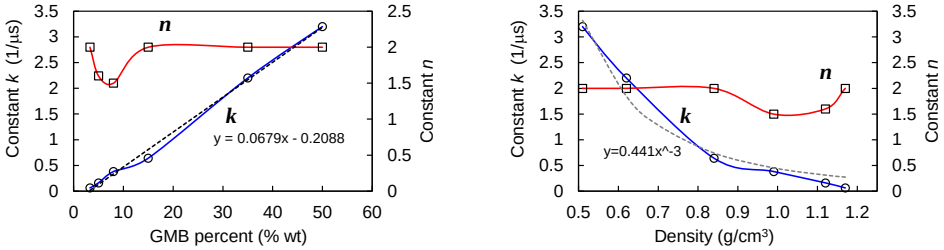

Figure 5. Effect of GMB percent (a) and density (b) on reaction rate constants

The obtained dependence of reaction rate constants *k* and *n* in pressure-based rate model can serve for rough estimation (initial guess) of values of rate constants for any GMB content in emulsion explosives. As described earlier (in Section 2.1), shock Hugoniot and equation of state of unreacted emulsion explosives can be also estimated using empirical equations that take into account effect of GMB content (i.e., density), while radial expansion can be estimated by empirical equation that takes into account charge radius and the failure radius. In this way, all input parameters required by the Wood-Kirkwood model can be roughly estimated by equations proposed in this work. This can greatly facilitate the calibration procedure of input parameters for emulsion explosives.

3 Conclusions

In this paper we present a model for theoretical calculation of detonation properties of low-density emulsion explosives, containing from 5 to 50% glass micro-balloons (over mass of emulsion matrix) and having densities between 1.12 and 0.51 g/cm^3. The model is based on the Wood-Kirkwood detonation theory, coupled with thermochemical code EXPLO5, and uses empirical equations to calculate the key input parameters such is radius of shock curvature and parameters in equation of state of unreacted explosive.

The rate of decomposition of emulsion explosive is described by pressure-based rate model, where the rate constants are calibrated using literature reported experimental detonation velocity-charge radius data for six emulsion explosives having different GMB content. It was shown that, when properly calibrated, the model satisfactorily reproduces experimental detonation velocity-charge radii and the failure radii data.

It was found that the rection rate constant (*k*) increases greatly with increase of GMB content, while the constant *n* (pressure exponent) varies from 1.5 and 2. The increase of reaction rate is consistent with the fact that GMB, as a sensitizer, plays significant role in initiation of emulsion explosives – they serves as hot-spots and increase of their content results in an increase of reaction rate in the early stage of decomposition. The constant *k* increases almost linearly with GMB percentage in the mixture, and such dependence can be used for rough estimation (initial guess) of *k* value for any GMB amount.

Acknowledgement

This work has been supported by Croatian Science Foundation (HRZZ) under the projects IP-2019-04-1618.

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