# Theoretical foundations of the implementation of controlled pyrotechnical reactions as an energy source for transportation from the sea bed

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## Abstract

The depletion of inland deposits of natural resources and the increasing demand for some raw materials have resulted in the growing interest in deep sea exploitation of natural deposits. This gives an impulse to the mounting research and development of methods of exploitation of natural deposits from the sea and ocean floors, which are not limited to petrol and gas. The main area of difficulty in opencast mining methods conducted at considerable depths is the transportation process from the sea floor to the surface. The methods employed so far, such as continuous line bucket (CLB), hydraulic pumping (HP) and air-lift pumping (ALP), have both advantages and disadvantages. The most salient problem is their considerable energy consumption resulting in great costs, hence the need for the development of less expensive methods. The authors have suggested a new method, involving the use of pyrotechnical materials as a source of energy in the transportation from the sea floor and have presented its theoretical grounding. Special emphasis has been placed on determining the depth to which the method can be applied and the energy needed in transportation in relation to the density of the transported substance (output).

## Introduction

Transport from the sea floor to the surface poses major difficulties when employing opencast marine mining at extreme depths. The solutions used to date (Karlic, 1984; Depowski et al., 1998), such as: CLB (continuous line bucket), HP (hydraulic pumping) or ALP (air-lift pumping) have proved to have their advantages and disadvantages. The biggest disadvantage is their energy consumption and, thus, high cost.

In this paper the authors want to present the use of pyrotechnical materials for the transport in water environment. The method is designed for the cyclical transport from big depths, over 200 meters. The transport module is based on the average alteration of density, which is inherently connected to the buoyant force affecting an immersed body. When the average density of the module is bigger than that of the surrounding medium, the buoyant force is lower than the weight of the body and the body falls down (sinks), whereas in the opposite case the buoyant force is higher than the body weight and the body emerges (floats). The situation in which the average density of the module equals the density of the surrounding medium is a particular case in which the buoyant force equals the body weight. In this condition, the body remains inert and floats in the liquid.

There are two ways in which we the average density of an immersed object can be changed. The first is used in submarines and is based on the use of ballast tanks, which, according to the need, are filled with water or emptied by using compressed air. The method is used when the depth does not exceed
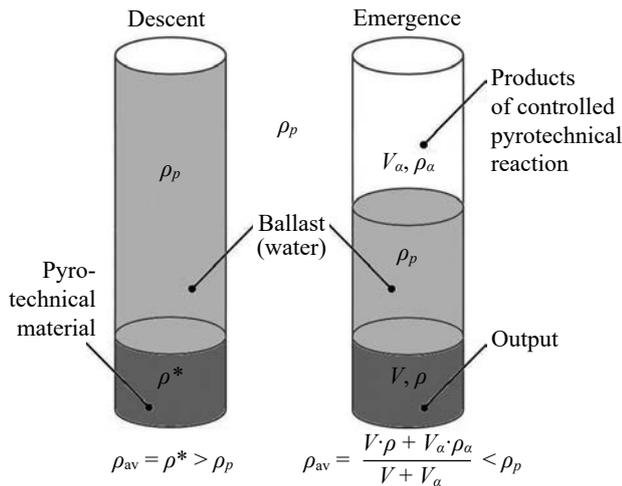
Figure 1. The concept of the implementation of controlled pyrotechnical reaction for transportation from sea bed



**Figure 2. The graph shows the relation between the growth of pressure ($p$) over time obtained during explosive deflagration time ($t$)**

several hundred meters. For technical reasons, this resurfacing method cannot be employed beyond depths of a few hundred meters and is it necessary drop the ballast, losing it irreversibly.

In order to present our concept of the use of pyrotechnic materials for transportation from the seabed (Figure 1) we show that, in the proposed solution, the weight of the structure of the transport unit does not change during either the descent to the bottom or the ascent to the surface. Therefore, in the following discussion we assume that we can balance the weight of the structure of the transport unit, affecting its buoyant force (Archimedean force). We focused on the processes taking place in the internal volume of the module, consisting of pyrotechnic material, having density $\rho^*$, and water, which acts as the ballast and whose density is indicated with $\rho_p$. In order for the module to descend, the density of the pyrotechnic material must be greater than the density of water. During the ascent, the volume occupied by the water will be then occupied by the gaseous products of the pyrotechnic reaction, having volume $V_\alpha$ and density $\rho_a$, which are pyrotechnic reaction products. The remaining volume $V$, of density $\rho_a$, is occupied by solid reaction products and the pyrotechnical output. The condition of emergence of the module is that the average density of the module, $\rho_{av}$, must be lower than $\rho_p$.

The pyrotechnical materials thus act as the energy source for the transport process, providing the energy input necessary to empty the ballast task. This concept is the subject of patented applications of the authors (Filipek & Broda, 2015a; 2015b). Through the research conducted to date, the authors have managed to devise a method for prolonging the deflagration method time of explosive materials belonging to the category of propellant explosives (powder).
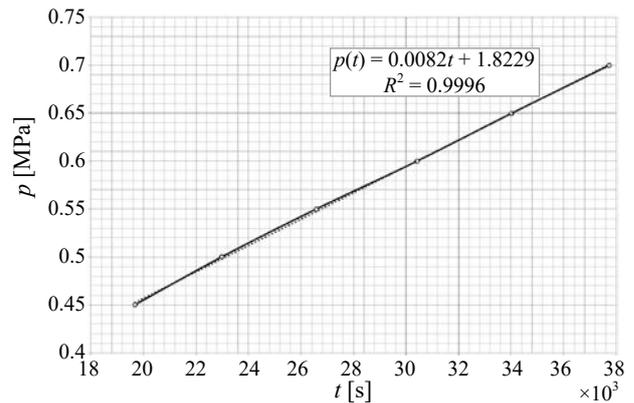
Experimental research shows that in order to decrease the abrupt pressure gradient, which is harmful to the application, it is necessary to prolong the time of the reaction that triggers the pressure increase. The shorter the combustion time is, the more abrupt the energy surge. As shown in Figure 2, it was possible to prolong the explosive deflagration time (the paper submitted for print by the authors).

Transport from the sea floor based on the use of pyrotechnical material is a complex system. In order to make the system fully operational it is vital to solve the problems concerning particular stages of utilization. As mentioned earlier, the research carried out to date has allowed to solve the problem of pressure increase in the pyrotechnical reaction. This was as indispensable step for the continuation of work. In the controlled pyrotechnical process, we achieved the possibility of carrying out a phase change from solid body (or fluid) to gas, obtaining the required parameters of pressure growth velocity, facilitating safe ballast tank emptying.

This paper focuses on the next stage of system operation – defining the maximum depth at which the transport system is fully operational. The way in which we sought to achieve the objective is shown in Figure 3. In the first step, we set the relationship enabling to determine the dependence of the energy needed to ascend from the depth $h$ (6).

In the second step, based on knowledge of potential energy, we determined the maximum $\rho_a$ value and the added $\gamma$ factor (10). We then analyzed the course of the controlled pyrotechnic reaction for the desired size (Step 3). Selected results are presented in Figures 5 and 6. In the last step, we focused on determining the maximum depth of

Step 1
Defining minimal energy necessary
for emergence from depth $h$

Step 2
Knowing the potential energy, we determine
the relations at the maximum $\rho_\alpha$ value

Step 3
We analyse how to determine density $\rho_\alpha$
from a known controlled pyrotechnic reaction

Step 4
We determine maximum depth of immersion
(hydrostatic pressure), at which the controlled
pyrotechnic reaction will enable to determine
the (assumed) $\rho_\alpha$ density value

**Figure 3. Algorithm for determining the maximum depth of immersion**

immersion (hydrostatic pressure) in correspondence of which it is possible to achieve emergence of the module without surpassing the maximum allowable density.

## Determination of conditions for preliminary considerations

In order to make the proposed method competitive against currently adopted solutions, it should be characterized by a higher energy efficiency. The minimum energy required to move a mass between two points in the gravitational field is determined by potential energy. It is this energy that we took as a reference point in our research. In order to accept the concept of free emergence of the body under the influence of buoyant forces, the work load of the gas must be determined. The pyrotechnical reaction product should be such that the value of the buoyant force can be bigger than the weight of the equipment.

The typical relation used for determining pressure at a given depth $h$ (1) (Halliday, Resnick & Walker, 2005; Orzechowski, Prywer & Zarzycki, 2009) is:

$$p = p_o + p_h = p_o + g \rho h \qquad (1)$$

Due to the fact that both the gravitational acceleration, $g$, and liquid density, $\rho_p$, are not constant values, the influence of these values on pressure should be taken into consideration and can be presented through the equation (2):

$$p = p_o + \int_0^H g(\varphi, h)\rho(s, T, h)\,\mathrm{d}h \qquad (2)$$

in which it was assumed that fluid density (Brahtz, 1974; Perry & Walker, 1982) is a function of three parameters: salinity ($s$), temperature ($T$) and depth ($h$). Gravitational acceleration, in turn, was determined by two parameters: latitude and distance from the center of the Earth. The relation between $g$ and latitude ($\varphi$) can be determined by (3) (Hinze, Frese & Saad, 2013):

$$g \approx \left( 9.7803267714 \frac{1 + 0.00193185138639\sin^2\varphi}{\sqrt{1 - 0.00669437999013\sin^2\varphi}} \right) \qquad (3)$$

where the spherical shape of the Earth was taken into consideration. However, because of the irregular structure of the lithosphere, the relations employed offer only approximate values of the gravitational acceleration. In order to determine pressure at a given depth, local anomalies have to be taken into consideration as shown in relation (4).

$$p = p_o + \int_0^H g(r, \varphi, \lambda)\rho(s, T, h)\,\mathrm{d}h \qquad (4)$$

In this equation, gravitational acceleration depends on three parameters: distance from the center of the Earth, $r$, and two parameters determining geographical position, namely $\varphi$ and $\lambda$.

It turns out that determining pressure distribution as a function of depth is practically impossible without data on the changes with altitude of the local fluid and of the local change of gravitational acceleration with depth. Thus, with a significant degree of approximation, we assumed as reference that a pressure of 1 bar corresponds to that of a 10 m column of water and thus the pressure of 100 bar corresponds to the pressure at the depth of 1 km.

$$1\,[\text{bar}] \approx 10\,\text{mH}_2\text{O} \approx 10^5\,[\text{Pa}]$$
$$100\,[\text{bar}] \approx 1\,\text{kmH}_2\text{O} \approx 10^7\,[\text{Pa}] \approx 10\,[\text{MPa}]$$

## Determining energy and buoyancy depending on density

Let us consider the work performed during the movement of weight of density $\rho$ from a certain depth, $h$, to the surface of liquid. Let us assume that weight lifting takes place in a non-viscous liquid of density $\rho_p$ in order not to consider the influence of flow resistance at emergence of the object in question. The amount of work performed to move the object in question can be expressed through the following relation (5):

$$\Delta E_p = W = mgh = ghV(\rho - \rho_p) \qquad (5)$$

where $V$ stands for the volume occupied by the object in question. Of course, equation (5) is only reasonable when the density of the lifted weight ($\rho$) is bigger than the density of the surrounding liquid ($\rho_p$). In the opposite case, the calculation of the work would be meaningless because the object would emerge on its own.

Now let us consider the work of the isobaric transformation which we would have to perform at the depth $h$ in order to change the density of the object in question by changing its volume. The initial volume and density of the object are, respectively, $V$ and $\rho$. The volume of liquid that has to be pumped into the object in order to increase its volume is $V_\alpha$ and its density is $\rho_\alpha$. The relation describing isobaric transformation takes the form of equation (6). Pressure $p$ at depth $h$ is going to be determined from relation (1) by subtracting ambient pressure $p_o$. Omitting ambient pressure in equation (6) results from the fact that we do not calculate absolute work but the work up to the moment of emergence of the object. Besides, the pumped-in liquid carries an energy equal to $p_o V_\alpha$, which, when subtracted from the absolute work, will give us the result described in equation (6).

$$W = pdV = p((V_\alpha + V) - V) = pV_\alpha = \rho_p g h V_\alpha \quad (6)$$

By comparing equations (5) and (6), we obtain the following:

$$V(\rho - \rho_p) = \rho_p V_\alpha \Rightarrow V_\alpha = V\left(\frac{\rho}{\rho_p} - 1\right) \quad (7)$$

Equation (7) carries the information on the maximum volume $V_\alpha$ when the theoretical work performed at depth $h$ equals the potential energy and thus coincides with the hypothetical work which would have to be performed for the surfacing of the object from depth $h$ if the work is performed in non-viscous fluid. Equation (7) does not provide, however, any information on whether the object will sink, float or emerge. In order know this, we have to evaluate the coefficient, marked as $n$, which is the multiplication factor in $V_\beta = nV$. This coefficient must be chosen so that the average density of the whole object is equal to the density $\rho_p$ of the surrounding liquid and is going to be determined from the inequality (8):

$$\frac{\rho_\alpha V_\beta + \rho V}{V_\beta + V} \leq \frac{\rho_p(V_\beta + V)}{V_\beta + V} = \rho_p \Bigg\} \Rightarrow n \geq \frac{\rho - \rho_p}{\rho_p - \rho_\alpha} \quad (8)$$

By putting into equation (7) the solution of the inequality (8) we will obtain relation (9):

$$\begin{aligned}\frac{V_\beta}{V_\alpha} &= n\frac{\rho_p}{\rho - \rho_p} \\ n &= \frac{\rho - \rho_p}{\rho_p - \rho_\alpha}\end{aligned}\Bigg\} \Rightarrow \frac{V_\beta}{V_\alpha} = \frac{\rho_p}{\rho_p - \rho_\alpha} \quad (9)$$

When analysing equation (9) it is easy to notice that the relationship $V_\beta/V_\alpha$ is actually the relationship between the theoretical work required to create a volume, $V_\beta$, filled with liquid of density $\rho_\alpha$ at depth $h$, and the hypothetical work which we would be required to take out the object in question from depth $h$ to the surface. By introducing the additional coefficient, $\gamma$, which is the relationship between $\rho_\alpha/\rho_p$, we will obtain the following expression (10):

$$\delta = \frac{V_\beta}{V_\alpha} = \frac{E}{E_p} = \frac{1}{1 - \gamma} \quad (10)$$

Equation (10) explains, inter alia, that the work performed in creating the volume $V_\beta$ at depth $h$ will be always bigger than the hypothetical work which we would have to be performed to extract the object from the depth $h$.

Figure 4, which is a graphic representation of equation (10), shows that a mutual correlation exists between the coefficients $\gamma$ and $\delta$ defined in the equation (10). In order to create an equation in which the work required to create a fluid-filled volume $V_\beta$ (fluid of $\rho_\alpha$, depth $h$), equals the potential energy $E_p$, assumed as a reference point, the value of $\rho_\alpha$ at the depth $h$ would have to amount to zero (vacuum). The more $\rho_\alpha$ approaches $\rho_p$, the more work has to be performed. This is justifiable because a higher value of $\rho_\alpha$ implies that a bigger volume $V_\beta$ must be generated so that the density of the whole object is at least equal to the one of the surrounding liquid.
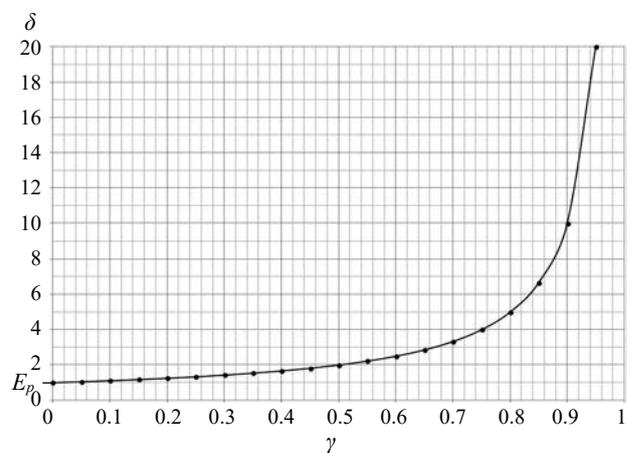


**Figure 4. Graphic interpretation of the dependence of $\delta$ on $\gamma$**

## Analysis of selected pyrotechnical reactions

By conducting research on pyrotechnic reactions (Błasiak, 1956; Urbański, 1985; McLean, 1992; Brown, 2000; Dyja, Maranda & Trębiński, 2001; Papliński, Surma & Dębski, 2009), we have learned to control their progress. The control of pyrotechnical reaction that its spontaneous (uncontrolled) course is not allowed. This enables us to eliminate, or significantly reduce, most products of combustion, typical of uncontrolled pyrotechnical reaction, e.g. $CO$, $CH_4$, $H_2$.

The solutions were based on three types of reactions taking place during the combustion of explosives:

$$4KNO_3 + 5C \rightarrow 2K_2CO_3 + 2N_2 + 3CO_2 \quad (11)$$

$$4KNO_3 + 5C \rightarrow 2K_2O + 2N_2 + 5CO_2 \quad (12)$$

$$C_8(NO_2)_8 \rightarrow 4N_2 + 8CO_2 \quad (13)$$
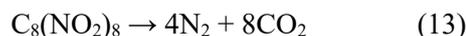
Reaction (11) is a typical deflagration reaction of the black powder without sulphur and with insignificant traces of chemical compounds resulting from combustion of charcoal. Pyrotechnical reaction (12) takes place in ordinary black powder deflagration; however, because of the considerable chemical affinity between potassium oxide and carbon dioxide, these compounds react with each other, resulting in reaction (11). When controlling the process, it is possible to favor reaction (12) while suppressing the secondary reaction between potassium oxide and carbon dioxide.

Reaction (13) is detonation of one of more modern explosives – octanitrocubane – and it is treated by the authors as a comparative reaction. It is unlikely to be used for our purpose because of the short detonation time (short duration ca. 10 km/s). However, the authors considered this reaction to be worth analyzing because there are two products of combustion: nitrogen and carbon dioxide.

Process analysis requires gathering all the physical and chemical data available in literature

$$4KNO_3 + 5C \rightarrow 2K_2CO_3 + 2N_2 + 3CO_2$$



$$4KNO_3 + 5C \rightarrow 2K_2O + 2N_2 + 5CO_2$$



$$C_8(NO_2)_8 \rightarrow 4N_2 + 8CO_2$$
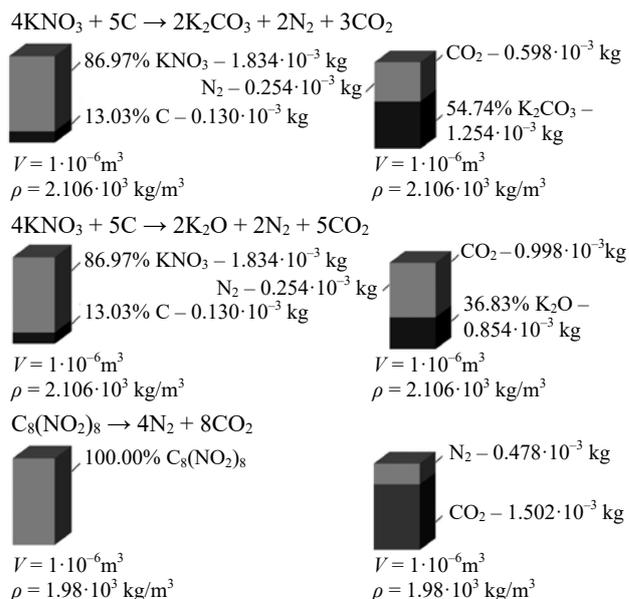


**Figure 5. Graphic illustration of mass balance of products and substrates for the three paths of pyrotechnic reactions in the case of immersion and emergence of the transportation module**

(Mizerski, 2013; Tablice fizyczno-astronomiczne, 2013; PubChem, 2016).

Figure 5 presents a graphical representation of pyrotechnical reactions for three courses of reaction (11), (12), (13). On the left-hand side of Figure 5, the input composition of the pyrotechnical material for each reaction, with the respective density, was presented. On the right-hand side, the products of reaction with percentage share of volume of the solid phase and weight share of the products are shown. These mass fraction, were the input point for further calculations after having been converted to moles.

In the analysis of the model, three states of aggregation were assumed. It was also assumed that potassium carbonate ($K_2CO_3$) from reaction (11) and potassium oxide ($K_2O$) from reaction (12) are present in the solid state. We also assumed, due to the lack of data in literature, that solid state is non-compressible (is not subject to compression) in comparison to other discussed phases and that $CO_2$ is always present in the liquid state. This assumption made us keep within the critical temperature limit

Table 1. Physical and chemical data of substances used for analysis

| Molecular formula | Potassium nitrate | Carbon | Octanitro-cubane | Potassium oxide | Potassium carbonate | Nitrogen | Carbon dioxide |
|---|---|---|---|---|---|---|---|
| | $KNO_3$ | $C$ | $C_8(NO_2)_8$ | $K_2O$ | $K_2CO_3$ | $N_2$ | $CO_2$ |
| Molar mass | 0.1011032 kg/mol | 0.0120107 kg/mol | 0.4641296 kg/mol | 0.094196 kg/mol | 0.138205 kg/mol | 0.0280134 kg/mol | 0.0440095 kg/mol |
| Density | $2.109 \cdot 10^3$ kg/m³ (20°C) | $2.09\text{–}2.23 \cdot 10^3$ kg/m³ | $1.98 \cdot 10^3$ kg/m³ | $2.32 \cdot 10^3$ kg/m³ (20°C) | $2.29 \cdot 10^3$ kg/m³ | | |

for $CO_2$, amounting to 30.98°C (304.15 K). The relationship between density change of the liquid phase and pressure function was determined on the basis of the equation as proposed by Span and Wagner (1996). An algorithm (EMS Energy Institute, 2015) (tool software) is available online to determine the density of the liquid phase as a function of pressure and temperature. We assumed, for the purpose of our research, that nitrogen is always in the gas phase. The change of the density as a function of pressure was determined from the Van der Waals equation (14) (Szargut, 2005):

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad (14)$$

where:

$n$ – amount of gas (in moles);
$V$ – volume (in $m^3$).

In our research, the following values were assumed (Mizerski, 2013; Tablice fizyczno-astronomiczne, 2013):

$R$ = 8.314462 J/(mol K) – universal gas constant;
$a$ = 0.141 $(J \cdot m^3)/mol^2$ – experimental constant – parameter of particle attraction;
$b$ = $3.91 \cdot 10^5$ $m^3/mol$ – experimental constant – volume excluded from the movement of particles.

## Determination of maximum pressure

An iterative method was applied to determine the immersed object density. The research excluded the construction mass because it can be balanced (buoyancy will be balanced at zero), for example by employing floats (tanks filled with oil). The calculations initially included the assumed density of the products resulting from reactions (11), (12), and (13). The following step involved the assumption of the temperature at which these densities should be determined. In most cases, this value was set at 5°C (278.16 K). We then determined pressure at

the interface between liquid $CO_2$ and gaseous $N_2$, assuming insolubility of one phase in the other. This pressure was determined with an accuracy of three decimal points, using iterative methods to solve the system of two equations consisting of the Van der Waals equation (14) for the gas phase and the EoS equation for the liquid phase.

Figure 6 presents the result of pressure determination, obtained when the density of the product of the three reactions amounted to 1 $g/cm^3$. The percentage share for each product was also shown for the reactions considered. We can conclude from Figure 6 that the maximum depth guaranteeing emergence depends heavily on the amount of solid phase in the reaction products. Therefore, the least beneficial result (21.9 MPa) equivalent to the depth of ca. 2.19 km can be obtained for the reaction (11). Far more beneficial is the case of reaction (12), characterized by a smaller share of the solid phase with a depth of ca. 3 km. The third course reaches the depth of ca. 21 km.

Figures 7 and 8 present the maximum obtainable pressure as a function of reaction product density (for three courses of reaction (11), (12), (13)).

All the curves were determined for the ambient temperature of 5°C (278 K). Moreover, the graphs with average product density of 1000 $kg/m^3$ show how the pressure will increase with temperature (empty circles on the graph correspond to temperature values 278 K, 283 K, 293 K, 303 K). Additionally, the curve depicting the relationship between maximum pressure and density is presented, relative to the condition in which the transport system works with clean carbon dioxide in the liquid phase and solid and liquid products are removed from the operational area of the device. The relationship between reaction product densities for a transport system working with clean nitrogen was not shown because of the excessively big values in the scale of figures. For instance, with an average density amounting to 0.6 $g/cm^3$, we obtain a maximum pressure value



$p$ = 21.9 MPa      $p$ = 30.4 MPa     $p$ = 210.6 MPa

45.81% $N_2$    36.91% $N_2$    41.00% $N_2$

28.20% $CO_2$    45.61% $CO_2$    59.00% $CO_2$

25.99% $K_2CO_3$    17.49% $K_2O$

$4KNO_3 + 5C \rightarrow 2K_2CO_3 + 2N_2 + 3CO_2$    $4KNO_3 + 5C \rightarrow 2K_2O + 2N_2 + 5CO_2$    $C_8(NO_2)_8 \rightarrow 4N_2 + 8CO_2$
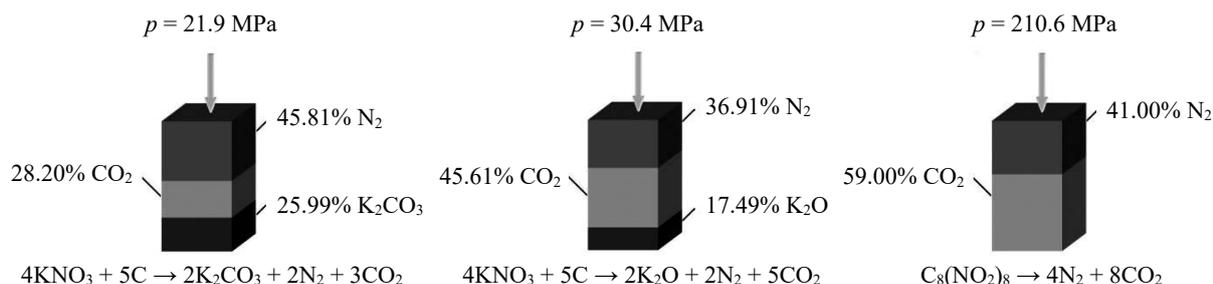
**Figure 6. Comparison of maximum pressures for three pyrotechnical reactions with the assumed average density of the reaction products equal to 1000 $kg/m^3$**
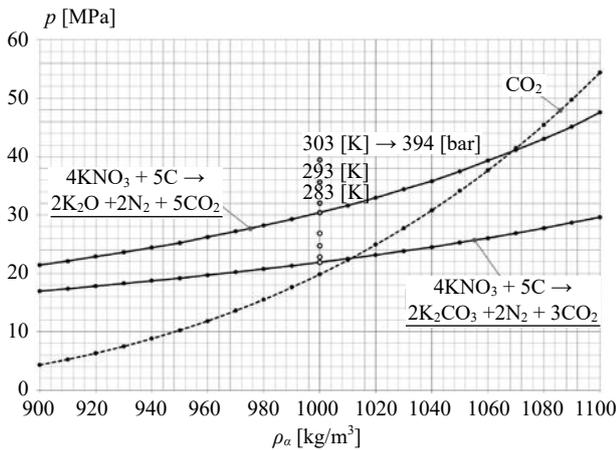
**Figure 7. Relationship between the maximum pressure $p$ and the product density $\rho_\alpha$ at $T = 278$ K for the first ($4KNO_3 + 5C \rightarrow 2K_2CO_3 + 2N_2 + 3CO_2$) and second ($4KNO_3 + 5C \rightarrow 2K_2O + 2N_2 + 5CO_2$) reactions and clean carbon dioxide**
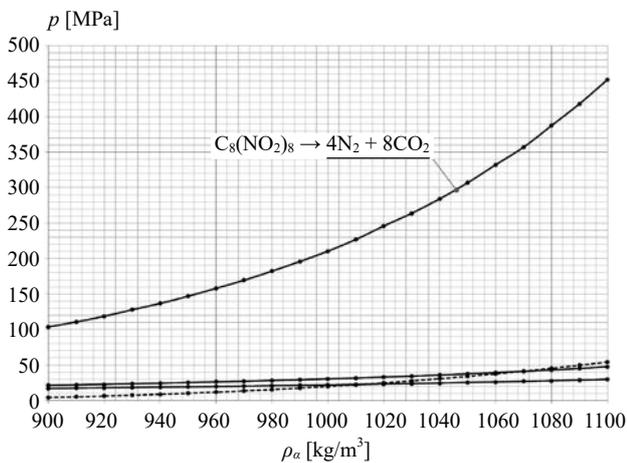


**Figure 8. Relationship between maximum pressure $p$ and density $\rho_\alpha$ for three reactions and clean carbon dioxide**
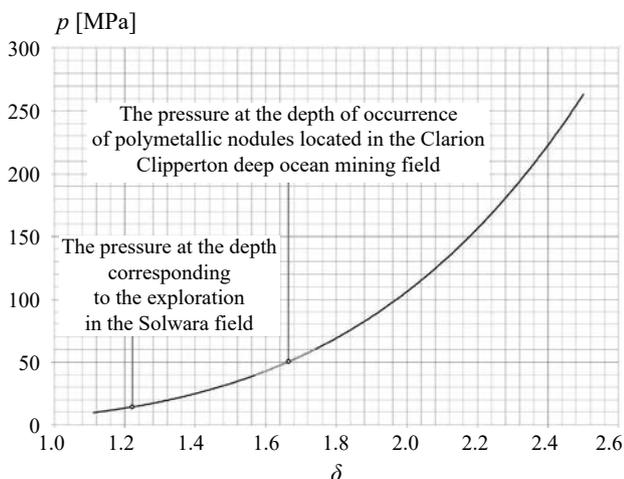


**Figure 9. Graph of relation of coefficient $\delta$ (energy consumption rate) and pressure $p$ for clean nitrogen $N_2$ determined for temperature $T = 278$ K**

of 261.5 MPa at the temperature 5°C (278 K), while the density scale assumed for our graphs starts with 900 kg/m$^3$.

By analyzing Figure 9, we can see that in the case in which the system works on clean nitrogen, the theoretical value of $\delta$ would not exceed two.

In any case, the authors of this publication claim that, except for the value of $\delta$ the most important point affecting the feasibility of this transport system is the cycle of storage and recovery with respect to the energy obtained from explosive deflagration. The efficiency of the process determines the future application of this method.

## Conclusions

From the analysis of the obtained pyrotechnical reaction products (Figures 6, 7, 8) we can conclude that the solid phase significantly limits the maximum pressure and thus the depth from which the system can get back to the surface. If, after emergence, solid reaction products were removed from the device, greater depths could be achieved thanks to the greater "supply" of potential energy.

On the basis of the discussions it can be concluded that the transport system should work with $CO_2$ and $N_2$ as working agents due to the fact that carbon dioxide is easily liquefied with increasing pressure and the system becomes more flexible in comparison to the system working on clean nitrogen.

In order to obtain maximum energy efficiency, the system should work at the lowest coefficient $\delta$, equal to 1; however, this case is theoretically impossible because vacuum conditions would have to be created. On the other hand, the density $\rho_\alpha$ should not be close to $\rho_p$ because, in this situation, $\delta$ approaches infinity.

The authors are aware of the possible impact of the proposed concept on the environment. At the current stage of research, the authors have reduced this impact by eliminating sulphur from the pyrotechnic material. Further investigations are being carried out and will be successively published.

## Acknowledgments

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