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ABOUT THE MISUSE OF THE DETONATION VELOCITY FOR THE CHARACTERIZATION OF HIGH EXPLOSIVES

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Abstract

In the characterization process of an explosive, there is a certain tendency to use the detonation velocity $D$ as the main parameter because it is easier to measure than the detonation pressure or energy, whereas the main quality generally required is a high release of mechanical energy during the expansion of the detonation products. These parameters are obviously correlated but not strictly related. Typical examples of discrepancies are presented and explained: adding water to a granular explosive (in order to fill the porosity) or adding hydrogen to the stoichiometric mixture $2H_2 + O_2$ (in condensed phases) increases $D$; adding inert solids to an explosive does not vary its detonation pressure if these solids can be considered incompressible. However, all these additions obviously decrease the specific energy of the explosive by dilution.

The last example emphasizes the importance of the compressibility of the detonation products: the greater this compressibility, the greater the specific energy of the explosive for a given value of $D$. This may suggest selection criteria for new explosive molecules, especially if used in shaped charges. Both this compressibility and the detonation energy are easily accessible experimentally by measuring the angles of expansion of these products on both sides of an explosive slab coated on one side and initiated at its end.

Résumé

Dans le processus de caractérisation d’un explosif, on a parfois tendance à utiliser la vitesse de détonation $D$ comme principal paramètre parce qu’elle est plus facile à mesurer que la pression ou l’énergie de détonation, alors que la principale qualité généralement requise est la fourniture d’une énergie mécanique importante pendant la détente des produits de détonation. Il existe évidemment une corrélation entre ces grandeurs, mais pas une relation stricte. Des exemples typiques de divergences sont présentés et expliqués : l’addition d’eau à un explosif granulaire (de façon à remplir la porosité) ou l’addition d’hydrogène au mélange stoïchiométrique $2H_2 + O_2$ (en phases condensées) accroît $D$ ; l’addition de solides inertes à un explosif ne modifie pas sa pression de détonation si ces solides peuvent être considérés comme incompressibles. Mais toutes ces additions diminuent évidemment l’énergie spécifique de l’explosif par dilution.

Le dernier exemple souligne l’importance de la compressibilité des produits de détonation: plus celle-ci est élevée, plus l’énergie spécifique de l’explosif est élevée pour une valeur donnée de $D$. Ceci peut suggérer des critères de sélection pour de nouvelles molécules explosives, spécialement pour un usage dans des charges creuses. Tant cette compressibilité que l’énergie de détonation sont facilement accessibles expérimentalement par mesure des angles de relèvement de ces produits sur les deux faces d’une plaque explosée recouverte sur une face et amorcée en bout.
1. **Introduction**

The following presentation is not the result of recent discoveries: just the contrary, it is the recall of some fundamental laws which sometimes appear to be forgotten by explosives scientists, not by ignorance but by excess of simplification. Namely, when characterizing an explosive, there is a certain tendency to use the detonation velocity \( D \) as the main parameter, even sometimes the only relevant parameter in addition to density. A high detonation velocity \( D \) may actually be a requirement per se in some cases (e.g. in explosive lenses which combine high and low values of \( D \)), but most often, the main quality required from a high explosive is:

- either a high detonation pressure \( p_{c1} \) if its purpose is to generate intense shock waves in the adjacent medium;
- or a high release of mechanical energy during the expansion of the detonation products if its purpose is to impart high kinetic energies to fragments or to shaped charge liners.

Characterizing high explosives by their detonation velocity is certainly reasonable as a first approximation because \( D \) appears as \( D^2 \) in the expressions of detonation pressures and energies and because \( D \) is much easier to measure experimentally than these pressures and energies. However, relying too much on this first approximation may lead to presenting erroneous statements in literature and possibly to committing development expenses to new materials which eventually prove disappointing.

This can be illustrated on three types of examples presented hereafter. Given the purpose of this paper, all these examples have been deliberately selected in publications already available in the early 1970s or even before.

2. **Examples of discrepancies**

2.a) **Adding water to a granular explosive**

Take a tube with a thin wall (in order to produce little confinement) and fill it with granular RDX or PETN: the density of the explosive is low and so is the detonation velocity \( D \). Now, repeat this experiment after pouring water into the tube so as to fill the intergranular spaces: the values now found for \( D \) are higher than without water: 7.08 km/s instead of 5.57 km/s for 42.7 vol% water in the case of PETN.
This obviously does not mean that the slurry is more energetic than dry granular RDX or PETN: water reacts very little with other detonation products, and anyhow that little reaction is endothermic. Assuming that reaction to be negligible, the slurry must have the same energy per volume as the dry granular explosive and a lower energy per mass.

2.b) Adding hydrogen to a stoichiometric hydrogen/oxygen cryogenic mixture

Take a stoichiometric hydrogen/oxygen mixture in the condensed state at 20°C and make it detonate. Experimental measurements are unprecise because the mixtures are heterogeneous (when hydrogen is liquid, oxygen is solid), but the detonation velocity as measured is ca. 5,000 m/s. Now, add excess hydrogen: this obviously reduces the energy per mass since that excess behaves as an inert diluent, but this increases the detonation velocity up to a maximum of 7,250 to 8,250 m/s for a mixture 9H₂ + O₂.

2.c) Adding inert solids to solid explosives

Take a solid explosive and add it 10 to 75% inert solids. The energy per mass of the mixture is logically proportional to the percentage of explosive (as is confirmed by Fig. 2 of Annex 1), but Table 1 shows that the corresponding detonation velocity only slightly decreases and the variations of the detonation pressure are within experimental errors (The mode of measurement of detonation energies and pressures is explained in Annex 1).

3. Analysis of discrepancies

These discrepancies show that the detonation velocity is not the only parameter governing detonation energies and pressures. Other important parameters are:
- the density of the explosive;
- the average molecular mass of its detonation products;
- the compressibility of these detonation products.

This is analyzed hereafter using very rough analytical approximations based on very simplified assumptions because their only purpose is to explain how these parameters influence D and pcr in three situations which all result in decreasing the energy by dilution. The legitimacy of these approximations results from acceptable correlations with experimental or accurately computed results.
3.a) Adding water to a granular explosive

The first approximation used is that proposed by Kamlet\(^{9}\) in 1968 for the detonation velocities and pressures of C-H-N-O explosives:

\[
D = A \Phi^{\gamma}(1 + B \rho_c) \quad \text{and} \quad \rho_{CJ} = K \Phi \rho_c^2
\]

where \(\rho_c\) is the density of the unreacted explosive, \(A\) and \(B\) are empirical coefficients and \(\Phi\) is a function of three thermochemical coefficients \(Q, G\) and \(M\):

\[
\Phi = GQ^3M^{-3}
\]

with

- \(Q\) the reaction enthalpy per mass of an arbitrary reaction which uses all the oxygen available into \(H_2O\), then into \(CO_2\) (excess \(C\) remaining unreacted);
- \(G\) the proportion of gas in the detonation products of that reaction (\(G = 1\) in the absence of condensed phases);
- \(M\) the average molecular mass of the gas phase.

In example (a), the detonation velocity of dry granular PETN is low because its density is low. Adding water decreases \(Q\) by dilution, but it improves the other three relevant factors:

- it increases the density \(\rho_c\) (water is not substituted for PETN but for intersticial air);
- it increases the proportion \(G\) of the gaseous phase in the detonation products;
- it decreases the average molecular mass of that phase by adding \(H_2O\) (\(M = 18\)) to a mixture of \(CO_2\) (\(M = 44\)) and \(N_2\) (\(M = 28\)).

The calculations of Annex 2 (# 2) show that filling voids with water actually increases not only \(D\) but also \(\rho_{CJ}\). The values calculated are slightly higher than the experimental ones\(^{9,10}\), which is normal since experiments are made with finite diameters while the critical diameter increases with additions of water, but the agreement remains quite acceptable even at porosities over 40 vol\%. Hence, assuming that the detonation energy per mass \(E\) of the real reaction is not too different from \(Q\) (arbitrary reaction), we have an example of a modification which results in the following evolution of the detonation parameters:

\[
D \rightarrow \rho_{CJ} \rightarrow E
\]
3.b) **Adding hydrogen to a stoichiometric hydrogen/oxygen cryogenic mixture**

The detonation velocity of the stoichiometric mixture $2\text{H}_2 + \text{O}_2$ is low in consideration of its energy per mass: this results from its very low density. Adding excess hydrogen has two negative effects on this detonation velocity, following Kamlet’s approximation:

- it decreases the density still further (due to the low density of liquid hydrogen);
- it slightly decreases the energy per mass (by dilution);

but it leaves $G$ unchanged ($G = 1$) and, over all, it strongly decreases $M$:

$$2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \quad \text{mass} = 36, \quad \text{number of moles} = 2, \quad M = 18$$

$$9 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + 7 \text{H}_2 \quad \text{mass} = 50, \quad \text{number of moles} = 9, \quad M = 5.55...$$

The detonation pressure was not measured in these experiments. Given the opposite influences of $\rho_c$ and $M$ on $p_{\text{CJ}}$, it is difficult to be conclusive. It remains that we have an example of a modification which results in the following evolution of the detonation parameters:

$$D \rightarrow E \rightarrow$$

3.c) **Adding inert solids to solid explosives**

Kamlet’s approximation does not extend to additions of inerts to explosives, so another theoretical approach must be adopted. This is described in Annex 2 (# 3) and shows that adding inert solids to a baseline explosive:

- does not vary its detonation pressure; and
- (with light additives) only slightly decreases its detonation velocity;

provided these additives can be considered as chemically and thermally inert and mechanically incompressible, and provided the detonation can still be treated as ideal. The ideal detonation assumption is not true with very dense additives (10) and the incompressibility assumption is clearly preposterous at CJ pressures. However, this assumption becomes more and more acceptable as pressure drops during the expansion of the detonation products, and as previously stated, the only purpose of these calculations is to show how the presence of additives influences $D$, $p_{\text{CJ}}$, and the specific energy $E$. Actually, the values for $p_{\text{CJ}}$ and for $D$ (with light additives) in Table 1 are in reasonable agreement with this theory. They show the following evolution of the detonation parameters:

$$D = \text{constant} \quad p_{\text{CJ}} = \text{constant} \quad E \rightarrow$$
4. **Influence of the compressibility of the detonation products**

This last example reveals the influence of the compressibility of the detonation products: taking it to the extreme shows that, if these were totally incompressible (e.g. produced by a reaction such as Al + Fe₂O₃ which is exothermal but which only produces solids), they would not deliver any mechanical energy during their "expansion". This influence is no recent discovery either: it always appeared in the expression of the specific energy E of a high explosive within the "polytropic" approximation (i.e. the assumption of a constant value \( \Gamma \) of the isentropic exponent \( \gamma = \partial \ln p / \partial \ln v \) as presented in Annex 2, # 4):

\[
E = D^2 / 2(\Gamma^2 - 1)
\]

Annex 1 shows how an approximation to \( \Gamma \) and to the value \( \gamma_{\text{ij}} \) can be calculated from simple experimental measurements, together with the maximum kinetic energy which an explosive can impart to an adjacent liner. Annex 2 (# 4) analyzes the relation between \( \Gamma \) and the compressibility of detonation products, in particular by addition of supposedly incompressible solids. Tables 1 and 2 confirm, in spite of the unrealism of the incompressibility assumption, that the average \( \Gamma \) as measured increases as higher proportions of solid phases (inert solid or reactive aluminum) are added. The high values reached by \( \gamma_{\text{ij}} \) show the error which can be made when characterizing an explosive (especially if aluminized) by the factor \( \rho_c D^2 / 4 \), as is often done, since this factor represents a fictitious detonation pressure based on the assumption \( \gamma_{\text{ij}} = 3 \) (see Eq. 2 of Annex 1).

Extending this rationale to C-H-N-O formulations suggests that reducing excess carbon should increase the compressibility of detonation products (i.e. decrease \( \Gamma \)), as seems the case when comparing TNT, TNB and picric acid in Table 3.

5. **Conclusions**

In conclusion, it has been shown that the detonation velocity \( D \), the detonation pressure \( \rho_{\text{ij}} \) and the specific detonation energy \( E \) are three parameters obviously correlated but not strictly related. so characterizing an explosive by \( D \) alone (or by \( \rho_c D^2 \) with \( \rho_c \) the density) may lead to erroneous conclusions.
Incidentally, the absence of a strict correlation between D and E can suggest a method of selection of explosives for shaped charges by seeking the best compromise between two not-totally-incompatible properties:

- obviously the highest possible E;
- but also a relatively low D so as to minimize the critical angle below which a conical liner does no longer form a jet, since for a given caliber of the warhead, the liner - hence the jet - is all the longer as this angle is smaller, all other factors being equal.

Among the parameters to be taken into account in addition to D, the compressibility of the detonation products plays an important role. This can also suggest a guidance for the research of new substances by favoring molecules which produce the lowest possible proportion of solid phase in the detonation products, e.g. high-nitrogen-low-carbon molecules. There is actually a strong interest in such molecules\(^{(11)(12)}\), but the values calculated for \(\gamma_{ij}\) are not very conclusive under that point of view, maybe because diatomic \(N_2\) is less compressible at low pressures than triatomic \(H_2O\) and \(CO_2\).

References
1. W. Kegler, A. Baumann - Unpublished results (1971)
7. M. Défourneaux - Transferts d’énergie dans la propulsion par explosif - Sciences et Techniques de l’Armement, fasc. 3 & 4-73 (1973)
Table 1 - Properties of explosives containing inert solids (in mass proportion \( r_s \))

<table>
<thead>
<tr>
<th>Baseline HE (%) by mass</th>
<th>Additive</th>
<th>Nature</th>
<th>( \rho_s ) (g/cc)</th>
<th>( r_s )</th>
<th>( \rho_c ) (g/cc)</th>
<th>D (km/s)</th>
<th>( \gamma_{cJ} )</th>
<th>( p_{cJ} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX/TNT 65/35</td>
<td>asbestos</td>
<td>2.85</td>
<td>0.10</td>
<td>1.70</td>
<td>1.800</td>
<td>7.885</td>
<td>(2.92)</td>
<td>(28.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.20</td>
<td>1.78</td>
<td>1.878</td>
<td>7.670</td>
<td>(2.94)</td>
<td>(28.1)</td>
</tr>
<tr>
<td>RDX/TNT 50/50</td>
<td>Al(_2)O(_3)</td>
<td>3.90</td>
<td>0.20</td>
<td>1.70</td>
<td>1.970</td>
<td>7.625</td>
<td>(2.78)</td>
<td>(30.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.30</td>
<td>1.82</td>
<td>1.928</td>
<td>7.218</td>
<td>(3.11)</td>
<td>(24.6)</td>
</tr>
<tr>
<td>RDX/TNT 42.7/57.3</td>
<td>Na(_2)SO(_4)</td>
<td>2.70</td>
<td>0.25</td>
<td>1.70</td>
<td>1.860</td>
<td>7.220</td>
<td>(2.92)</td>
<td>(24.8)</td>
</tr>
<tr>
<td>PETN/Silicone 63.5/36.5</td>
<td>Bi(_2)O(_3)</td>
<td>8.9</td>
<td>0.641</td>
<td>3.07</td>
<td>4.798</td>
<td>5.65</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>WC</td>
<td>15.1</td>
<td>0.50</td>
<td>2.56</td>
<td>4.652</td>
<td>4.71</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.625</td>
<td>3.187</td>
<td>4.204</td>
<td>4.98</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.75</td>
<td>4.34</td>
<td>3.734</td>
<td>5.65</td>
<td>10.7</td>
<td></td>
</tr>
</tbody>
</table>

. Data with RDX/TNT baseline explosives: From Ref. 6 - Average \( \Gamma \) deduced from measurements of \( \phi_0 \) (Eq. 1 of Annex 1) - \( p_{cJ} \) and \( \gamma_{cJ} \) calculated using Eq. 2 and 4 of Annex 1.

. Data with PETN/Silicone baseline explosive: From Ref. 5 - D, \( p_{cJ} \) and \( \gamma_{cJ} \) computed using BKW code - Results on baseline explosive not given.

Table 2 - Influence of solid phases on the compressibility of detonation products

<table>
<thead>
<tr>
<th>Formulation (% by mass)</th>
<th>-</th>
<th>Compressibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETN</td>
<td>( \phi_0 ) (measured)</td>
<td>( \Gamma ) (deducted from ( \phi_0 ) )</td>
</tr>
<tr>
<td>80 Polyurethane 20 Al 00</td>
<td>35° 00°</td>
<td>2.84</td>
</tr>
<tr>
<td>40 Polyurethane 40 Al 20</td>
<td>28° 28°</td>
<td>3.42</td>
</tr>
<tr>
<td>20 Polyurethane 25 Al 55</td>
<td>20° 13°</td>
<td>4.73</td>
</tr>
</tbody>
</table>

. Data: From Ref. 6 - Average \( \Gamma \) calculated using Eq. 1 of Annex 1

Table 3 - Evolution of \( \gamma_{cJ} \) with excess carbon in trinitrobenzene and derivatives

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Formula</th>
<th>( \rho_c ) (g/cc)</th>
<th>D (km/s)</th>
<th>( p_{cJ} ) (GPa)</th>
<th>( \gamma_{cJ} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>( [C_nH_{3(n-1)}(NO_2)_{n-1}]CH_3 )</td>
<td>1.637</td>
<td>6.94</td>
<td>18.9</td>
<td>3.17</td>
</tr>
<tr>
<td>TNB</td>
<td>( [C_nH_{3(n-1)}(NO_2)_{n-1}]H )</td>
<td>1.64</td>
<td>7.27</td>
<td>21.9</td>
<td>2.96</td>
</tr>
<tr>
<td>Picric acid</td>
<td>( [C_nH_{3(n-1)}(NO_2)_{n-1}]OH )</td>
<td>1.76</td>
<td>7.57</td>
<td>26.5</td>
<td>2.81</td>
</tr>
</tbody>
</table>

. Data: From various sources in literature.
Annex 1 - The Plate-Push Test as a Means of Characterizing High Explosives

Many different geometries can be adopted to experimentally measure the kinetic energy imparted by a high explosive to a coating. The main ones are:

- the closed symmetrical geometry of the "cylinder test" where an explosive rod is totally surrounded by its coating, hence the detonation products can only expand laterally by pushing that coating until it is totally fragmented;

- the open unsymmetrical geometry of the "plate-push" test(8) where an explosive slab is coated on one face only, hence the detonation products can expand freely on the unconfined face while pushing the coating on the confined one (Fig. 1).

The cylinder test is representative of divergent explosions such as detonations of shells or bombs; it was the first one to appear and remains the most used. The plate-push test was developed to simulate the primary projection of shaped charge liners; it is more recent and less used, but it presents several advantages:

- the velocity of the coating can be obtained by a measurement of the detonation velocity D combined with a single flash radiograph giving the angle $\phi$ of lateral deflection of the coating (Fig. 1);

- the outcome of the test is independent of the nature of the liner, since this does not withstand any stretching nor fragmentation as it does in the cylinder test;

- the test measures an energy which has an intrinsic meaning, namely the maximum kinetic energy which can be imparted to a coating per unit mass of the explosive in an open geometry: this maximum (called "ballistic capacity" and denoted CB) would be equal to one third the specific energy E of the explosive if the lateral dimensions of the slab were infinite;

- in addition to that "ballistic capacity" the flash radiograph used for the measurement of $\phi$ also gives access to an average value $\Gamma$ of the isentropic coefficient $\gamma$ of the detonation products, by measuring the angle $\phi_0$ of free expansion of the detonation products on the unconfined face (which can be made easily visible with a very thin metal sheet). Indeed, in the polytropic approximation ($\Gamma$ = constant):

\[
\phi_0 = \frac{\pi}{2} \left( \frac{\Gamma + 1}{\Gamma - 1} - 1 \right)
\]  (1)

If $\Gamma$ were really constant from its initial value $\gamma_{ij}$ in the detonation front to its end value at low pressure, knowing D and $\Gamma$ would allow the calculation of the detonation pressure $p_{ij}$ and provide another approach to the specific energy E, using the following equations (with $\rho_e$ the density):

\[
p_{ij} = \rho_e D^2 / (\gamma_{ij} + 1)
\]  (2)

\[
E = D^2 / 2(\Gamma^2 - 1)
\]  (3)
Using Eq. (2) requires either accepting the lack of precision of the polytropic approximation or finding a better correlation between the average $\Gamma$ of Eq. (1) and the value $\gamma_{ij}$ of Eq. (2). An acceptable correlation was found\(^{(8)}\), and is used for the calculation of $p_C$ in Table (3) of the main text of this paper:

$$\frac{(\Gamma + 1)}{(\gamma_{ij} + 1)} \approx 0.95 \quad (4)$$

Eq. (3) has no practical interest since the plate-push test provides a direct access to a specific energy CB, and also to a volumetric energy CBV = $p_c$ CB which presents a good correlation with the energy measured in the cylinder test\(^{(8)}\). Fig. 2 shows in particular that, as is logical, CB decreases proportionally to $(1 - r_a)$ when a mass proportion $r_a$ of an inert additive is added to a baseline explosive (denoted with the subscript $b$):

$$CB = (1 - r_a) CB_b$$

However, Eq. (3) presents the interest of confirming that the detonation velocity is not sufficient to characterize a high explosive: indeed, for a given value of $D$, the energy $E$ is all the lower as $\Gamma$ is greater, i.e. as the compressibility of the detonation products is lower. This occurs in particular when incompressible inert solids are added to a baseline explosive without substantially modifying its detonation velocity (see Annex 2, # 4).

**Fig. 1 - The plate-push test**

**Fig. 2 - Influence of inert additives of the "ballistic capacity" CB of high explosives**

$(r_a = \text{mass proportion of additive}, CB_b = \text{value of CB for the baseline explosive})$
Annex 2 - Effect of inert additives on the detonation characteristics of explosives.

1. Relations between masses, volumes and densities

Symbols used:
- \( m = \) mass, \( V = \) real volume, \( \nu = \) specific volume,
- \( \rho = \) specific mass (density),
- \( p = \) pressure, \( D = \) detonation velocity

Subscripts:
- \( a = \) additive, \( b = \) baseline explosive,
- \( e = \) unreacted explosive, \( CJ = \) Chapman-Jouguet state

No subscript:
- explosive mixture (baseline explosive + additive)

Add a mass \( m_a \) of a substance A to a mass \( m_b \) of a baseline explosive in order to form an explosive mixture of total mass \( m \). In the unreacted mixture and at any stage of the expansion of its detonation products, the mass \( m \) occupies a total volume \( V \) with a density \( \rho \) corresponding to a specific volume \( \nu \). Using the same letters with subscripts \( a \) (for the additive alone) and \( b \) (for the baseline explosive alone) leads to the following relations:

\[
\begin{align*}
  m_a &= m_a m \\
  V_a &= \nu_a V_a / m_a = 1/\rho_a \\
  V_b &= \nu_b V_b / m_b = 1/\rho_b \\
  m_a &= (1 - r_a) m \\
  V_a &= (1 - s_a) V \\
  \nu_a &= (1 - r_a) \nu \\
  \nu_b &= (1 - s_a) \nu \\
\end{align*}
\]

where masses and mass ratios are constants whereas volumes (except for the additive) and volume ratios are functions of pressure. Considering the relations between \( V, \nu, m \) and \( \rho \):

\[
\begin{align*}
  \nu &= V/m = 1/\rho \\
  \nu_a &= V_a / m_a = 1/\rho_a \\
  \nu_b &= V_b / m_b = 1/\rho_b
\end{align*}
\]

it follows that:

\[
\begin{align*}
  \rho / \rho_a &= \nu_a / \nu = V_a / V , \quad m / m_a = s_a / r_a \\
  \rho / \rho_b &= \nu_b / \nu = V_b / V , \quad m / m_b = (1 - s_a) / (1 - r_a)
\end{align*}
\]

\[
\begin{align*}
  \rho / \rho_a &= s_a / r_a \\
  \rho / \rho_b &= (1 - s_a) / (1 - r_a)
\end{align*}
\]

Eliminating \( s_a \) or \( r_a \) between these two equations gives two expressions valid in all states, including the unreacted state and the CJ state:

\[
\begin{align*}
  \rho &= s_a \rho_a + (1 - s_a) \rho_b \\
  \nu &= r_a \nu_a + (1 - r_a) \nu_b
\end{align*}
\]

(1)

Assuming the additive to be chemically inert, the total chemical energy of the mixture is only that of the baseline explosive, i.e. a proportion \( (1 - r_a) \) of the mixture (as confirmed by Fig. 2 of Annex 1). Hence, in terms of specific energies \( E \) (i.e. energies per mass unit):

\[
E = E_{\text{unreacted explosive mixture}} - E_{\text{detonation products at } \rho = \eta} = (1 - r_a) E_b
\]

(2)

(note that energies and enthalpies are identical for the solid unreacted explosive and for the detonation products at zero pressure).
2. **Additions of Water to Granular PETN**

Using solid PETN as the baseline explosive (molecular mass \( m_e = 316 \), theoretical density \( \rho_{eb} = 1.77 \)), replace a volume proportion \( s_a \) of PETN with either air or water and calculate \( D \) and \( p_{CJ} \). As a first approximation, and for qualitative purposes only, this can be done by using Kamlet's approximation based on the following arbitrary reaction:

\[
C_2H_8N_4O_{12} \rightarrow 2 N_2 + 4 H_2O + 4 CO_2 + C \quad \Delta H = - Q_b = -1525 \text{ cal/g}
\]

which gives 10 moles of gas representing a mass of 304 g out of the total of 316. Hence:

\[
G_b = 304/316 \quad \text{and} \quad M_b = 304/10
\]

In the first case (porosity), the chemical reaction is unchanged so the parameters \( Q, G \) and \( M \) - hence \( \phi \) - remain constant and only the density varies:

\[
\phi = \phi_b \quad \rho_c = (1 - s_a) \rho_{eb}
\]

In the second case, the volume proportion \( s_a \) of water corresponds to the addition of \( n \) moles of water (mass \( m_w = 18n \)) per mole of PETN (\( m_e = 316 \)), so the reaction becomes:

\[
C_2H_8N_4O_{12} + n H_2O \rightarrow 2 N_2 + (4 + n) H_2O + 4 CO_2 + C \quad \Delta H = - Q = - (1 - r_a) Q_b
\]

with

\[
r_a = \frac{18n}{316 + 18n} \quad \frac{1}{s_a} = 1 + \frac{316\rho_a}{18n \rho_{eb}}
\]

\[
G = \frac{304 + 18n}{316 + 18n} \quad M = \frac{304 + 18n}{10 + n}
\]

Using the numerical values \( A = 1.01, B = 1.3 \) and \( K = 1.558 \) allows us to calculate \( D \) and \( p_{CJ} \) and compare the additions of water and air at equal volume proportion \( s_a \). The results are given below:

<table>
<thead>
<tr>
<th>( s_a )</th>
<th>( n ) (moles)</th>
<th>PETN + water</th>
<th>PETN + air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( D ) (km/s)</td>
<td>( p_{CJ} ) (GPa)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>8.70</td>
<td>33.3</td>
</tr>
<tr>
<td>0.169</td>
<td>2</td>
<td>8.20</td>
<td>28.2</td>
</tr>
<tr>
<td>0.289</td>
<td>4</td>
<td>7.81</td>
<td>24.6</td>
</tr>
<tr>
<td>0.427</td>
<td>7.4</td>
<td>7.32</td>
<td>20.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( s_a )</th>
<th>PETN + water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D ) (km/s)</td>
</tr>
<tr>
<td>0</td>
<td>7.08 (^{3)} )</td>
</tr>
</tbody>
</table>

*Experimental data:* From Ref. 3 - value with \( \rho_c = 1.441 \), PETN fully wetted, \( \phi \) 25 mm

From Ref. 2 - correlation \( D = 3.19 + 3.7(\rho_c - 0.37) \) with \( \rho_c = 1.014 \)
3. **Additions of incompressible inert solids**

Assume now that:
- the additive is chemically inert, thermally inert (no heat transfer) and mechanically inert (no compression energy);
- the mixture is homogeneous and remains so during the expansion of the detonation products.

The total mechanical energy per mass released by the detonation products during their expansion from \(p_{CJ}\) to 0 is exclusively provided by the baseline explosive, i.e. by a proportion \((1 - r_a)\) of the mixture. Hence, in terms of specific energies \(E_{CJ}\):

\[
E_{CJ} = \int_{v_a}^{v_m} pv = (1 - r_a) E_{CJ,b}
\]

Hence:

\[
E_{CJ} - E = (1 - r_a) (E_{CJ,b} - E_b)
\] (3)

The CJ theory relates each of these two differences with the detonation pressure \(p_{CJ}\), the specific volume \(v_{CJ}\) of the detonation products and the specific volume \(v_e\) of the unreacted explosives (baseline and mixture), as follows:

\[
E_{CJ} - E = \frac{1}{2} p_{CJ} (v_e - v_{CJ}) \quad \text{and} \quad E_{CJ,b} - E_b = \frac{1}{2} p_{CJ,b} (v_{e,b} - v_{CJ,b})
\]

Eliminating the energies by means of Eq. (3) gives:

\[
p_{CJ} (v_e - v_{CJ}) = p_{CJ,b} (1 - r_a) (v_{e,b} - v_{CJ,b})
\] (4)

Since Eq. (1) is applicable to both the unreacted state and the CJ state, it follows that:

\[
v_e = r_a v_a + (1 - r_a) v_{e,b} \quad \text{and} \quad v_{CJ} = r_a v_a + (1 - r_a) v_{CJ,b}
\]

hence:

\[
v_e - v_{CJ} = (1 - r_a) (v_{e,b} - v_{CJ,b})
\] (5)

Combining Eq. (4) and (5) gives:

\[
p_{CJ} = p_{CJ,b}
\] (6)

which means that adding a solid, assumed incompressible and inert, to a baseline explosive does not modify its detonation pressure.

From this equality it is easy to calculate the effect of the additive on the detonation velocity, using another relation of the CJ theory for both the mixture and the baseline explosive:

\[
p_{CJ} = \rho_e D_e^2 \left(1 - \frac{\rho_e}{\rho_{CJ}}\right) = \rho_e D_e^2 (v_e - v_{CJ})
\]

\[
p_{CJ,b} = \rho_{e,b} D_b^2 \left(1 - \frac{\rho_{e,b}}{\rho_{CJ,b}}\right) = \rho_{e,b} D_b^2 (v_{e,b} - v_{CJ,b})
\]
Using Equations (5) and (6) gives:

\[ \frac{p_{CI}}{p_{CI,b}} = (1 - r_a) \frac{\rho_c^2 D^2}{\rho_{eb}^2 D_b^2} = 1 \]

Applying Eq. (1) to the unreacted explosives (baseline and mixed) gives a relation between the corresponding detonation velocities:

\[ D/D_b = (1 - r_a)^{\gamma_b} \frac{\rho_{eb}}{\rho_c} = (1 - r_a)^{\gamma_b} [r_a \frac{\rho_{eb}}{\rho_a} + (1 - r_a)] \]  

(7)

If \( \rho_a \) (density of the additive) were equal to \( \rho_{eb} \) (density of the baseline explosive), this equation shows that the presence of the additive would increase the detonation velocity. Conversely, if \( \rho_a > \rho_{eb} \) (e.g. for Bi₂O₃ and WC in Table 2 of the main text), then \( D < D_b \). In between, inert additives can have little effect on \( D \), while obviously decreasing \( E \) according to Eq. (2).

4. Compressibility of the Detonation Products

This result evidences the influence of the compressibility of the reaction products, which is all the lower as the proportion of incompressible additive is higher. This compressibility can be characterized by the isentropic exponent \( \gamma \) of the detonation products as they expand (\( \gamma \) is all the greater as the compressibility is smaller):

\[ \gamma = - \left( \frac{\partial \ln p}{\partial \ln v}_s \right) = - \left( \frac{\partial p/p}{\partial v/v}_s \right) = (- \frac{\partial p/p}{\partial v/v}_s) \frac{(v/v}_b) (\partial v_b/\partial v)_s \]

Among the three factors of this last expression, the first one is the isentropic exponent \( \gamma_b \) of the detonation products of the baseline explosive, the second one is given by Eq. (1) and the third one results from the derivation of that equation. Since \( r_a \) and \( v_a \) remain constant during the expansion, this derivation gives:

\[ (\partial v_b/\partial v)_s = (1 - r_a) \]

Hence:

\[ \gamma = \gamma_b \frac{r_a v_a / v_b + (1 - r_a)}{(1 - r_a)} = \gamma_b \left[ \frac{r_a}{1 - r_a} \cdot \frac{v_a}{v_b} + 1 \right] \]

This expression actually shows that \( \gamma \) is an increasing function of the proportion \( r_a \) of additive and of its specific volume \( v_a \). When applied to the CJ state, \( v_b \) must be replaced by \( v_{CI,b} \) and the equation takes a different form (which can be deduced directly from the expression of \( p_{CI} \) as a function of \( \gamma_{CI} \), given by Eq. 2 of Annex 1):

\[ \frac{\gamma_{CI} + 1}{\gamma_{CI,b} + 1} = \frac{r_a}{1 - r_a} \cdot \frac{v_a}{v_b} + 1 \]

Annex 1 provides an experimental access to an average value of \( \gamma \).