The Challenge of Non-Ideal Detonation

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Abstract : This paper will compare and contrast detonation in ideal and in highly non-ideal explosives. Ideal explosives, represented here by a TATB / binder system, have relatively flat velocity of detonation (VoD) versus inverse charge diameter relationships, and fail at VoDs only slightly below their ideal CJ values. Highly non-ideal explosives, such as the physically heterogeneous composites used both in Naval and in mining applications, display more complex VoD relationships, and greater deficits at failure. Indeed, the example chosen here of an ANFO / emulsion blend has a bi-linear diameter effect curve, with the VoD at failure being only 30% of its CJ value. These behaviours are interpreted by examining their reaction rate surfaces (namely the 3D relationship between pressure, extent of reaction and reaction rate). Many of the experimental tests in common use, and many models of the detonation process, rely on particular features of the reaction rate surface that are specific to ideal explosives. Such features are modified or absent from the surfaces for highly non-ideal explosives, with the result that the experimental tests can become either misleading or irrelevant, while the theoretical models are inappropriate.

1. INTRODUCTION

A casual glance through the collected indexes [1] of the first eight Symposia (International) on Detonation is sufficient to show that detonics research over the last four decades has concentrated overwhelmingly on the behaviour of explosives developed for applications which demand the highest possible power generation. Together with the secondary criteria of stability and sensitivity [2], this has narrowed attention down to about half a dozen high density monomolecular explosives, and mixtures thereof, all of which exhibit fast reaction kinetics under detonation conditions. As a result of this concentration of effort, the majority of the experimental techniques and the theoretical models that have been developed and applied over this time period have implicitly assumed the "ideal" type of detonation behaviour that is exhibited by these explosives.

However, there are other applications that apply different selection criteria to the choice of explosive composition. Naval underwater explosives are formulated to provide moderate pressures of long pulse duration, often by the addition of aluminium. Energetic propellants (based on ammonium perchlorate) must deflagrate stably at low pressure without transiting to a detonation that they are also capable of supporting. Mining explosives must detonate at low pressure with long pulse duration to avoid excess

pulverisation but still provide sufficient fracture and movement of large rock masses : as such, modern compositions are usually based on ammonium nitrate. All of these different composite explosive types exhibit long reaction zones even under detonation conditions, resulting in pronounced “non-ideal” behaviour, where detonation is strongly influenced by the charge size and external confinement.

It is then essential to verify that any experimental technique or theoretical model proven with ideal explosives is still valid when applied to non-ideal explosives.

As an example, Kennedy and Jones [3] examined the detonics of the Naval explosive PBXN-111 (formerly PBXW-115), concluding that (i) the extraction of detonation zone lengths from shockfront curvature measurements, (ii) run distance to detonation data, and (iii) a small-sample technique [4] for measurement of infinite diameter detonation velocity, all required different interpretation for this non-ideal explosive, compared to what would be the case for an ideal one. However, this analysis was based on a CJ detonation velocity predicted by a chemical equilibrium code [5] to be $0.5 \text{ mm} \cdot \mu\text{s}^{-1}$ higher than the infinite diameter value inferred from a linear extrapolation of the experimental detonation velocity data [6]. This makes its diameter effect curve (the dependence of steady-state detonation velocity D on charge diameter d in cylindrical geometry) concave up when plotted in the D vs d^{-1} plane, unlike those of ideal explosives which are usually linear or concave down, as summarised by Campbell and Engelke [7].

This paper will examine the detonics of a highly non-ideal explosive which has a pronounced and well-defined concave up diameter effect curve. It is known in the mining industry as a heavy ANFO (henceforth called HANFO), being an ICI proprietary blend of porous ammonium nitrate (AN) prill plus fuel oil (FO) mixed with an AN/water-in-oil emulsion.

Its detonics will be contrasted to those of X-0219 (90/10 TATB/KelF 800) which displays essentially ideal behaviour. X-0219 was chosen partly because of the completeness of the necessary experimental data, but also partly because TATB-based explosives are believed to have the longest reaction zone lengths of any ideal composition.

2. REACTIVE EQUATION OF STATE MODEL

The reactive equation of state (EoS) has been modified slightly from that used previously by Kennedy and Jones [3] to model PBXW-115 (now renamed PBXN-111), and extended to incorporate the effects of initial porosity.

2.1 Unreacted explosive

The unreacted or explosive phase is described by a Mie-Grüneisen EoS in the form

$$e_x = e_r + \frac{(p_x - p_r)}{\rho_{r0}\Gamma_{r0}} \quad (1)$$

where p is pressure, ρ is density, $v = \rho^{-1}$ is specific volume, e is specific internal energy, and Γ is the Grüneisen coefficient. The subscripts are: x for the (porous) unreacted explosive, 0 for the initial state, and r for the reference (non-porous) state. Formerly [3], the latter was represented by the principle isentrope for the non-porous condensed phase, given by the Birch-Murnaghan finite strain equation in the form described by Jeanloz [8]. This was found to work well with materials for which the slope s_r of the Hugoniot, given by :

$$U = C_{r0} + s_r u \quad (2)$$

where U is shock velocity and u particle velocity, is moderately low in value, say $s_r \leq 1.6$. This condition holds for the geophysical materials studied by Jeanloz [8]. However, for more compressible materials such as the AN / water based emulsions of interest here, the Hugoniot slope is greater, typically $s_r \geq 2.0$, and it was found that the Mie-Grüneisen EoS centred on the Birch-Murnaghan principle isentrope was not consistent with equation (2) for physical values of the Grüneisen coefficient Γ_{r0} .

The reference state for equation (1) is now the shock Hugoniot of the condensed phase, so that

$$p_r = \frac{\rho_{r0} C_{r0}^2 \phi}{(1 - s_r \phi)^2} \quad \text{and} \quad e_r = \frac{p_r \phi}{2 \rho_{r0}} \quad \text{where} \quad \phi = 1 - \rho_{r0} v_r \quad (3)$$

In order to treat initial porosity in the unreacted explosive, it is then necessary to relate v_r to v_x . This is performed here by assuming that the porosity is fully removed by compression at some low pressure to some specified specific volume, v_{comp} (where $v_{comp} < v_{x0}$). Then, under shock compression :

$$\left. \begin{aligned} v_r &= v_{comp} + \left(\frac{v_{r0} - v_{comp}}{v_{x0} - v_{comp}} \right) (v_x - v_{comp}) & \text{for } v_{comp} < v_x \leq v_{x0} \\ v_r &= v_x & \text{for } v_x \leq v_{comp} \end{aligned} \right\} \quad (4)$$

The pressures developed by detonating explosives are sufficient to always cause complete compaction, so that in all subsequent flow, $v_r = v_x$.

2.2 Reacted products

The reacted or product phase, denoted by the subscript p , is described by a polytropic EoS with a density-dependent index, namely

$$e_p = \frac{p_p v_p}{\gamma_p - 1} - q_p \quad \text{where} \quad \gamma_p = \gamma_0 + \gamma_1 \rho_p + \gamma_2 \rho_p^2 \quad (5)$$

and where q_p is the heat of reaction. The γ_i constants in equation (5) are determined by requiring that the correct values for $(\partial \ln p / \partial \ln v)_s$ are returned at the CJ state and at infinite expansion. These are taken from ICF's chemical equilibrium code IDeX (standing for Ideal Detonation of eXplosives), based on an intermolecular EOS [5] for the gaseous products and the Murnaghan EoS for the solid products

2.3 Mixture rules

The equation of state for the reacting mixture is then completed by invoking the simple mixture rules

$$p \equiv p_x \equiv p_p, \quad v \equiv v_x \equiv v_p, \quad e = (1 - \lambda) e_x + \lambda e_p \quad (6)$$

where λ is the extent of reaction, varying from 0 for the unreacted explosive to 1 for the detonation products. These rules will be discussed later.

2.4 Reaction rate law

The reaction rate law that controls the global energy release was originally developed for non-ideal composite porous explosives by Kirby and Leiper [9]. In order to describe the behaviour of ideal explosives such as X-0219, it has been necessary to increase the pressure dependency by allowing pressure exponents greater than unity, giving :

$$\dot{\lambda} = (1 - \lambda) \left\{ \frac{p_{hs}^{R_h} a_h}{\tau_h} + \frac{p^{R_i} a_i}{\tau_i} + \frac{p^{R_f} a_f}{\tau_f} \right\} \quad (7)$$

where

$$p_{hs} = \begin{cases} \frac{p}{4} \left(\frac{3p}{4p_{cr}} \right)^3 & \text{for } p < 4p_{cr}/3 \\ p - p_{cr} & \text{for } p \geq 4p_{cr}/3 \end{cases} \quad (8)$$

The subscripts are: h for hotspot, i for intermediate, and f for final stages of the reaction. Apart from the three power exponents R , there are four main adjustable parameters — three characteristic reaction times τ , and the critical pressure p_{cr} that inhibits the onset of the hotspot reaction.

The a factors in equation (7) describe the assumed geometry of the burn front, controlling the switching on and off of the hotspot, intermediate and final reaction rate terms. They are functions of λ , and are Gaussian in shape, namely

$$a_h = \exp \left\{ -[(\lambda - C_i)/W_h]^2 \right\}, \quad a_i = 0, \quad a_f = 0 \quad \text{for } 0 \leq \lambda \leq C_i$$

$$a_h = \exp\left\{-\left[(\lambda - C_i)/W_i\right]^2\right\}, a_i = 1 - a_h, a_f = 0 \quad \text{for } C_i < \lambda \leq C_f \quad (9)$$

$$a_h = \exp\left\{-\left[(\lambda - C_i)/W_i\right]^2\right\}, a_i = \exp\left\{-\left[(\lambda - C_f)/W_f\right]^2\right\} - a_h, a_f = 1 - a_h - a_i \quad \text{for } C_f < \lambda \leq 1$$

where the Gaussian parameters are defined in terms of the mass fractions, Φ , of the three stages as:

Centroids	$\begin{cases} C_i = \Phi_h^2 \\ C_f = (\Phi_h + \Phi_i)^2 \end{cases}$	Half-widths	$\begin{cases} W_h = 2C_i/(1 + C_i) \\ W_i = \Phi_h(1 - \Phi_h) \\ W_f = \Phi_f(1 - \Phi_f) \end{cases} \quad (10)$
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3. HYDRODYNAMIC MODELS

The above reactive equation of state was embedded into both the finite element hydrocode DYNA2D [10], and ICT's non-ideal detonation code CPeX (standing for Commercial Performance of eXplosives). The latter was developed to describe the detonics of non-ideal composite explosives by Kirby and Leiper [9], who extended the small divergent detonation theory of Wood and Kirkwood [11]. It describes the flow along the central streamtube between the detonation front and the sonic point (henceforth referred to as the WK point) for steady detonation in unconfined cylindrical geometry (henceforth referred to as WK detonation) by using the shooting method described by Braithwaite et al. [12] to solve the system of ordinary differential equations including the Euler equations of motion, the reactive equation of state, and the reaction rate law. Since the equations of motion have been restricted to the axis, the solution is incomplete, and requires an empirical relationship between the shock front curvature R_s and the charge diameter d . The following simple form has been found adequate for many types of explosives :

$$\frac{d}{R_s} = \alpha + \beta \frac{d_f}{d} \quad (11)$$

where α and β are empirical constants and d_f is the failure diameter. Chaissé et al. [13] have derived a similar expression from their transverse analysis of the physical variables at detonation fronts.

4. MODEL CALIBRATION

CPeX was calibrated for each explosive by varying the adjustable parameters in the reaction rate law, equation (7), until the predicted variation of detonation velocity with unconfined charge diameter matched the experimental measurements shown in Figure 1(a), constrained by the curvature relationships of equation (11) shown in Figure 1(b).

For HANFO, both the detonation velocities and the shockfront curvature data were measured by Sheahan [14], with the ideal detonation velocity D_{CJ} as predicted by IDeX [5]. Figure 1 also includes the results of DYNA2D simulations of the rate stick experiments. This diameter effect curve displays non-ideality on a larger scale than any previously published, with the detonation velocity at failure being only about 30% of the predicted CJ value. The inflection point at $d_f/d \approx 0.4$ is sharper than in the only other cases reported of upward curvature [14 and 15], dividing the diameter effect curve neatly into a small diameter and a large diameter branch. If the detonation velocity experiments had been performed only on the small diameter branch ($d_f < d < 2d_f$), the measurements would have displayed a linear dependence between D and d^{-1} with a correlation coefficient of $r^2 = 0.997$, though the extrapolated D_∞ would be lower than D_{CJ} by $1.65 \text{ mm.}\mu\text{s}^{-1}$. The large diameter branch is seen to extrapolate smoothly towards the predicted D_{CJ} , though the measured detonation velocity in the largest charge tested (250mm in diameter and 1500mm in length) is still $1.35 \text{ mm.}\mu\text{s}^{-1}$ below D_{CJ} .

For X-0219, the detonation velocities are those tabulated by Gibbs and Popolato [16], with the shockfront radii of curvature from Campbell and Engelke [7]. The ideal detonation velocity predicted by IDeX [5] was $7.775 \text{ mm.}\mu\text{s}^{-1}$, slightly higher than the value of $7.630 \text{ mm.}\mu\text{s}^{-1}$ from a linear extrapolation of the diameter effect curve. The latter was adopted for the fitting procedure. The reaction rate law for X-0219 was further constrained so that DYNA2D simulations of wedge tests reproduced the LASL Pop-plot

Figure 1. Fits to the experimental diameter effect data (left) constrained by the shockfront radii of curvature data (right) for X-0219 and HANFO. Both abscissa have been normalised by multiplying the inverse diameters by the respective failure diameters of 14mm and 46mm. For the diameter effect curve (left), the ordinate has been normalised by dividing the detonation velocities by the predicted CJ velocities of $7.630 \text{ mm} \cdot \mu\text{s}^{-1}$ and $5.807 \text{ mm} \cdot \mu\text{s}^{-1}$ respectively.

results [16] shown in Figure 2. For reasons to be discussed below, DYNA2D simulations could not be performed for rate stick experiments on X-0219.

In spite of the paucity of experimental shockfront radii of curvature for HANFO, it is evident that the shockfronts in HANFO are considerably more curved (i.e. smaller radii of curvature by a factor of roughly three) than their counterparts in X-0219 over the full range of charge diameters. The HANFO shockfronts are also more curved than those of the non-ideal explosive PBXN-111 [3], though are almost identical when normalised as in equation (11) to those of emulsion explosives with a range of initial densities and failure diameters [17].

5. FEATURES OF THE WK POINT

Figure 3 displays how the CPeX values of various flow variables at the WK point vary with charge diameter for X-0219 and for HANFO. In view of the dissimilar diameter effect curves and shockfront

Figure 2. Comparison between the experimental Pop-plot [16] for X-0219 and the results of DYNA2D simulations using the reaction rate surface shown in Figure 8(a).

Figure 3. CPeX flow variables at the WK point of steady detonation in unconfined cylindrical charges of X-0219 and HANFO. The inverse diameters have been normalised by multiplying by the respective failure diameters of 14mm and 46mm. The pressures in 3(c) have been normalised by dividing by the CJ pressures of 26.3 and 8.87 GPa respectively, while the densities in 3(d) have been normalised by dividing by the initial densities of the explosives, which are 1.915 g.cm⁻³ and 1.04 g.cm⁻³ respectively.

curvatures, it is not surprising that the related flow variables for the two explosives also exhibit large and significant differences.

Figure 3(b) examines the expansion of the central streamtube, chosen to have unit area at the shock front. This expansion is small ($< 2\%$) for the X-0219 but large ($\approx 30\%$) for the HANFO close to the failure diameter. Since this streamtube expansion is directly related to w_r (the radial partial derivative of the radial particle velocity), and since Wood and Kirkwood [11] expanded their correction terms to the conservation equations only to first order in w_r , it is pertinent to examine the accuracy with which CPeX can treat HANFO.

6. ACCURACY OF CPEX AND COMPARISON WITH DYNA2D

6.1 HANFO

It can be seen that CPeX is able to accurately reproduce both diameter effect curves in Figure 1, even the complex shape exhibited by the HANFO. However, of course, this does not verify CPeX, since the reaction rate parameters were varied until these fits were achieved. Unfortunately, there is insufficient experimental data currently available to independently test the CPeX analysis of HANFO.

When CPeX was applied to the non-ideal explosive PBXN-111 [3], the derived reaction rate surface could be used in DYNA2D simulations to accurately reproduce a wide variety of experimental data probing both steady and non-steady flows. However, this success will not necessarily translate to the present situation, because the CPeX central streamtube expansion at the failure diameter of PBXN-111 was only 4%.

For the present purpose, the only recourse is to compare the CPeX analysis with the results of DYNA2D simulations. While not providing an independent test of the reactive equation of state model, any demonstrated agreement between CPeX and DYNA2D would help confirm at least the broad features of the CPeX flow divergence model.

In this context, the high degree of accuracy with which the DYNA2D simulations (included in Figure 1) reproduce the CPeX detonation velocities and assumed shockfront radii of curvature relationship for HANFO is gratifying. As well as reproducing these gross features of detonation in rate stick geometry, the DYNA2D simulations also confirmed the fine structure in the CPeX analysis, such as the complex dependence of WK detonation zone length on charge diameter shown in Figure 3(f).

A further example is illustrated in Figure 4(b), displaying the predicted pressure and extent of reaction profiles along the axis for steady detonation in a 61mm diameter unconfined charge of HANFO — similar

Figure 4. Pressure and extent of reaction profiles for steady detonation. For X-0219 (left), the DYNA2D profiles are after the detonation has run 150mm in planar 1D geometry, while the CPeX profiles are for WK detonation in a 220mm diameter rate stick. For HANFO (right), all profiles are for a 61mm diameter rate stick.

agreement between CPeX and DYNA2D occurred over the full range of diameters. The finite element simulation of Figure 4(b) used a uniform mesh with $0.5\text{mm} \times 0.5\text{mm}$ elements, which at first glance may appear very coarse but in fact gives 61 elements across the radius of the charge, and about 22 elements in the detonation zone within which only about 35% reaction occurs.

6.2 X-0219

Figure 4 includes a comparison of CPeX and DYNA2D results for detonation in X-0219. The CPeX profiles are for WK detonation in 220mm diameter, which was the largest diameter for which CPeX could find a solution — this is taken to represent $\text{WK}(\infty)$. The DYNA2D simulation was performed with boundary conditions which restricted the flow to planar 1D geometry. The simulation was started by a programmed burn (with a free rear boundary) through a 50mm slab of X-0219, followed by a resolved reactive flow calculation through a 125mm slab of X-0219. It can be seen that the two approaches are in excellent agreement with each other.

This finite element simulation employed a uniform mesh with $0.01\text{mm} \times 0.01\text{mm}$ elements. Roughly 60% of the reaction (namely from $\lambda \approx 0.1$ to $\lambda \approx 0.7$) is predicted to occur over a zone of about 0.2mm in length, necessitating this high spatial resolution. The simulation of the rate stick experiments (with a minimum charge size of say 16mm diameter by 100mm length) would require at least 7 million elements to properly resolve the reaction, and since this was not feasible during this study, no 2D simulations could be performed on X-0219.

7. ACCURACY OF THE EQUATION OF STATE

Figure 5 summarises steady detonation in the p - v plane for these explosives, with the solid lines pertaining to 1D and the dot-dash lines to 2D. As described by Wood and Kirkwood [11], the radial divergence in a 2D detonation perturbs the Rayleigh “line” away from its linear 1D form, so that in 2D, the von Neumann spike, the WK (sonic) point and the point representing the initial undisturbed explosive are no longer co-linear.

For X-0219, this perturbation is small, and indeed is not readily apparent on the scale of Figure 5(a). All of the WK points are close to the CJ point, and hence for example, using the CJ product isentrope

Figure 5. p - v diagrams for steady detonation in X-0219 (left) and HANFO (right). The solid lines show the shock Hugoniot, the Rayleigh lines and the CJ product isentropes for 1D ZND detonation in these explosives, while the dot-dash lines show the reactive paths followed by 2D WK detonation in the largest and smallest diameters investigated experimentally.

predicted by a chemical equilibrium code to describe the isentrope in a WK detonation should not introduce significant additional error. Conversely, the JWL product equation of state determined in a copper tube expansion test, thus notionally under WK conditions, can be used to provide a reasonable description of the CJ state for explosives like X-0219.

This is not the case for HANFO, where the perturbations are significant. Indeed, for detonation in diameters close to the failure diameter, the specific volume at the WK point is expanded relative to the initial specific volume of the unreacted explosive — Figure 3(d) displays this in more detail. Furthermore, it is obvious that the state (including entropy, internal energy and temperature) of the shocked explosive behind the WK detonation front of a 51mm diameter charge will be vastly different from that behind a ZND detonation front. This will lead to a different set of product chemical species, so that basing the reactive equation of state (as described in section 2) only on the CJ product isentrope calculated by a chemical equilibrium code must be appreciably in error.

Johnson et al. [18] recognised this problem during their study of the performance of non-ideal ANFO + aluminium systems in the aquarium test. They treated some fraction of the ammonium nitrate (AN) as inert in their chemical equilibrium calculations using BKW, varying this fraction until the resulting predicted CJ velocity matched the experimental WK velocity for the particular geometry of interest. The remaining AN was then assumed to react outside the detonation zone. This procedure should lead to a more relevant equation of state than is used in the present study, though is still not rigorous due to the arbitrary treatment of the reaction and to the extent by which the 2D WK points lie off their equivalent 1D Rayleigh lines.

The p - v relationships shown in Figure 5 for WK detonation refer to conditions along the axis of symmetry. The uncertainties in treating the reactive equation of state are magnified at the edges of the detonating charges. Figure 6 presents contour plots generated by a DYNA2D simulation of detonation in a 51mm diameter unconfined charge of HANFO, this being only marginally larger than the failure diameter of 46mm. Figure 6(b) illustrates that there is an outer zone of about 5mm in thickness where the extent of reaction remains frozen at 25% or less. As can be seen from the plot of relative volume $\rho_0 v$ in Figure 6(d), the shockfront fully compacts the initially porous explosive, and it is the compressibility of this compacted material that largely controls the expansion of the outer inert zone and hence ultimately the radial divergence of the whole flow. Thus it is the case that the DYNA2D simulations of detonations close to failure are more sensitive to the details of the release isentrope of an initially porous material than they are to the reacted product isentrope.

Figure 6. DYNA2D simulation of detonation in a 51mm diameter charge of HANFO. The displayed segments are 50mm in length, with the detonation having run 300mm from the plane wave initiator. Both radial and axial axes are plotted on the same scale. The numbers under each label denote the contour interval. The location of the WK point is identified on plot (c), being where $u+c=D$, with u being the axial component of the particle velocity and c the sound speed.

The discussion to date has assumed that a shock Hugoniot is well defined for HANFO, by treating it as a homogeneous continuum. This assumption turns out to be incorrect.

The ammonium nitrate prills manufactured for incorporation in heavy ANFOs are typically 2 to 3 mm in diameter, and contain sufficient voidage to reduce their bulk density from its crystal value of 1.73 g.cm^{-3} down to roughly 1.33 g.cm^{-3} . The density of the AN/water-in-oil emulsion is also roughly 1.33 g.cm^{-3} , but being non-porous has a different compressibility from the prills. This difference in compressibility on the macroscopic scale of the heavy ANFOs gives rise to considerable shock focussing and dispersion. This is illustrated in Figure 7, which shows a DYNA2D simulation of the instantaneous pressure field in a regular array of AN prills with the layers separated by emulsion. (Being a 2D simulation, the prills are represented as infinitely long cylinders rather than as spheres.) In this simulation, both components are treated as completely unreactive, in order to examine the approach to pressure equilibrium. The lower boundary is being driven at $1 \text{ mm.}\mu\text{s}^{-1}$, which in an intimate mixture of the two components would give rise to a pressure of 4.25 GPa following the treatment of Afanasenkov et al. [19], where it is assumed that the two components are in pressure equilibrium and with each compressed to its respective shock Hugoniot volume. The pressure versus distance profiles exhibit excursions of up to 50% away from the continuum model pressure. In true 3D geometry and in lower density heavy ANFO compositions where the extra voidage is present as macroscopic air bubbles in the emulsion phase, these excursions are expected to be magnified even further. The pressure oscillations persist over distance scales of 20 to 30 mm, which from Figure 3(f) is comparable to typical detonation zone lengths for these explosives.

Hence, it is the case that pressure equilibrium does not exist even between the components of the unreacted phase, and so the unreacted equation of state must be understood to apply only in a very average sense. The mixing rules of section 2.3 were adopted with this in mind. In particular, requiring that the specific volumes of the unreacted and product phases remain equal is nonphysical, but greatly

Figure 7. DYNA2D simulation of a shockwave propagating through a 63/37 mixture of inert porous AN prills and emulsion in slab geometry. The lower boundary is being driven upwards at $1 \text{ mm.}\mu\text{s}^{-1}$, giving an average pressure of 4.25 GPa. The left hand plot shows the pressure field in an area of $6 \text{ mm} \times 12 \text{ mm}$ in size, while the right hand plot records the pressure versus distance profiles at the indicated locations.

Figure 8. Reaction rate surfaces for X-0219 (upper) and HANFO (lower) determined from the CPeX fits to the diameter effect curves of Figure 1. The contour plots show lines of constant reaction rate, plotted at $0.5 \mu\text{s}^{-1}$ intervals for X-0219 and at $0.02 \mu\text{s}^{-1}$ intervals for HANFO. Superimposed over each contour surface are firstly the dashed line traced out by the $(p(t), \lambda(t))$ histories between the shock front and the CJ point of a ZND detonation, secondly its 2D analogues in the largest (dot-dash) and smallest (dot) diameters investigated experimentally, and finally the solid line traced out by the $(p(d), \lambda(d))$ pairs at the WK point as the diameter is increased from its critical value (left hand end) to infinite diameter (right hand end) for steady detonation in unconfined cylindrical charges.

simplifies the solution algorithms.

A full rigorous solution to the theoretical problems described in this section lies beyond the scope of this paper.

The scale of the physical heterogeneity indicated in Figure 7 also introduces significant challenges to the experimentalist. The irregularities in the shock front preclude accurate measurements of the radii of curvature in 2D detonations. Any embedded pressure or particle velocity gauge needs to be long enough to average across a representative sample of the explosive, but the resulting high shear generated during the differential collapse of the two phases would cause gauge breakup well before the 8 to 12 μs timescale required to sample the end of the detonation zone as shown in Figure 3(e).

8. REACTION RATE SURFACE DIAGRAM

Once the adjustable parameters in equation (7) have been fixed for a given explosive, it can be seen that this reaction rate law describes a unique 3D surface in $(p, \lambda, \dot{\lambda})$ space. Such surfaces can be represented in a variety of graphical forms — it has been found most informative to display them as contour plots with pressure p and extent of reaction λ as the independent axes, and the contour lines representing the dependent $\dot{\lambda}$. Figure 8 presents the reaction rate surfaces necessary to reproduce the experimental diameter effect curves of Figure 1 using the CPeX reactive equation of state and divergent flow models. The pressure axis, for which $\lambda = 0$, corresponds to the conditions at the shock front.

Superimposed over these contour plots are line diagrams defining the regimes in which steady 1D and 2D detonation can occur.

Note that the contour interval for X-0219 is 25 times larger than that for HANFO.

8.1 X-0219

The reaction rate surface divides into four broad regimes along the pressure axis.

- Over the range $0 \leq p < 8$ GPa, $\dot{\lambda} \approx 0$ and X-0219 is essentially inert.
- Over the range $8 \leq p < 16$ GPa, $\dot{\lambda}(\lambda \approx 0)$ is small, and $\partial \dot{\lambda} / \partial \lambda > \partial \dot{\lambda} / \partial p$. Under these conditions, a sustained shockwave will propagate at steady or weakly accelerating velocity, until reaction at the rear boundary reaches $\lambda \approx 0.2$ and the reaction rate increases. This positive feedback situation generates a pressure excursion at the rear boundary, which eventually overtakes the initial shock taking it into the fourth regime discussed below. Hence, experimental wedge tests [16] conducted in this pressure regime would provide sharp shock to detonation transitions, with the traces of shock position versus

Figure 9. DYNA2D pressure profiles for sustained shock initiation in 1D planar geometry, following impact by a thick aluminium flyers at the left hand boundary. The profiles are shown at 0.25 μs intervals for X-0219, and at 4.0 μs intervals for HANFO. The dashed line on the back plane shows the shock pressure recorded at each distance.

time showing distinct low velocity and high (detonation) velocity regimes. Figure 9(a) exemplifies this.

- Over the range $16 \leq p < 24$ GPa, $\dot{\lambda}(\lambda \approx 0)$ is moderate, and $\partial\dot{\lambda}/\partial p > \partial\dot{\lambda}/\partial\lambda$. Any shock in this regime will show strong acceleration at the front, and a rapid transfer into the next regime. The shock position versus time traces observed in a wedge test will be curved, so the transition to detonation is diffuse.
- For $p \geq 24$ GPa, both $\dot{\lambda}(\lambda \approx 0)$ and $\partial\dot{\lambda}/\partial p$ are large. Any shock will quickly accelerate as far to the right of the pressure axis as the energy balance will permit.

This surface may be interpreted physically in a qualitative fashion. Over the first pressure regime, hotspot creation is inefficient, and thermal diffusion quenches reaction. Over the second regime, a limited volume of the shocked explosive is ignited by the formation of a small number of hotspots — the overall reaction rate eventually increases as the burn fronts grow geometrically. In the fourth high pressure regime, a large volume of the explosive is ignited by an increased variety of different hotspot mechanisms, giving the peak reaction rates at or just behind the shock. The third regime is transitional.

It is the resulting strong state dependence of the reaction rate law (i.e. large $\partial\dot{\lambda}/\partial p$ gradients at detonation pressures) that restricts the 2D WK detonation histories to a narrow band of pressures close to the ZND history. It is the high reaction rates within this band (i.e. $\dot{\lambda}(p \approx 34 \text{ GPa})$ is large) that force the reaction almost to completion within the detonation zone.

It is the large difference, a factor of roughly 100 to 500 in the absolute reaction rates between the low pressure regime, $8 \leq p < 16$ GPa, and the high pressure regime, $p \approx 34$ GPa, that makes it meaningful to ascribe shock initiation, with its associated Pop-plot [16], to the former and detonation to the latter.

8.2 HANFO

The reaction rate surface for HANFO shown in Figure 8(b) bears little resemblance to that discussed for X-0219. It does not divide into different pressure regimes, but instead, into different λ regimes. This is the result of control over the hotspot formation mechanisms (via the distribution of voidage) and the reliance on mass diffusion to limit reaction rates (via the physical separation between oxidiser and fuel phases).

Because of mass diffusion, the state dependence of the reaction rate law is weak (i.e. small $\partial\dot{\lambda}/\partial p$ gradients everywhere) and the absolute reaction rates are slow. The former makes it possible to sustain 2D detonation over a wide range of pressures. The latter allows the reaction to be incomplete within the WK detonation zone, since it becomes possible to satisfy the second WK condition [11], requiring the rate of energy production at the sonic point to match the radial expansion, at $\lambda < 1$.

Figure 9 compares initiation in HANFO to that in X-0219. The DYNA2D simulations were performed assuming planar 1D flow, starting at the time when a thick flyer plate impacts the left hand boundary. The flyer velocities were chosen so that the initial reaction rates for both explosives were equal, namely $\dot{\lambda} = 0.01 \mu\text{s}^{-1}$. For the HANFO, $\partial\dot{\lambda}/\partial p > \partial\dot{\lambda}/\partial\lambda$, and so the pressure accelerates at the shock front. However, both the gradients $\partial\dot{\lambda}/\partial p$, $\partial\dot{\lambda}/\partial\lambda$ and the absolute rate $\dot{\lambda}$ are small everywhere, so the acceleration is weak. It may be noted that the detonation has not reached steady state even after 500mm of run. From his perturbation method study of a model explosive with a late slow reaction, Bdzil [20] concluded that detonation in such explosives would indeed exhibit only very slow approach to steady state in 1D planar geometry. To examine this further, a second simulation was performed replacing the flyer plate by 200mm of detonating Composition B, with the results shown in Figure 10. Even after the detonation in the HANFO has run 500mm, the DYNA2D pressure versus distance profile has still not reached the equivalent profile predicted by CPeX for a 25m diameter charge (taken to represent infinite diameter). It may confidently be concluded that no current facility in the world could perform a 1D experiment on a sufficient scale to probe the CJ state of HANFO.

There is some structure evident in the trace of the shock pressure versus distance of Figure 9(b) which would translate into similar structure in shock velocity versus distance, but to extract shock to detonation

Figure 10. Pressure and extent of reaction profiles for HANFO. The DYNA2D profiles, for 1D planar geometry, are after the detonation has run 200mm and 500mm through the HANFO, following initiation by a programmed burn through 200mm of Composition B. The CPeX profiles are for WK detonation in 25m diameter (assumed to represent infinite diameter).

transitions from this structure would be inappropriate. Indeed, HANFO can detonate at this initial pressure provided its shockfront is sufficiently curved. In this type of non-ideal explosive, the difference between shock initiation and detonation lies in the geometry of the shockfront, not in its pressure. A Pop-plot cannot be defined for HANFO because the topography of its reaction rate surface does not provide the positive feedback mechanism that leads to shock-to-detonation transitions. The same is true of the emulsion investigated by Lee et al. [21], whilst PBXN-111 has a Pop-plot in the low pressure regime but not at intermediate pressures [3].

8.3 Accuracy of the reaction rate surface

The calibration procedure described in section 4 compensates to some degree for the errors in the divergent flow model discussed in sections 5 and 6, and for the errors in the reactive equation of state model discussed in section 7. This reduces the physical significance of the reaction rate law, making its fitted parameters strongly dependent on the models adopted.

Even with more rigorous models, there would remain uncertainties in the reaction rate surfaces that are inherent in the calibration procedure. When fitting a diameter effect curve, the solution is strongly dependent upon both the rate $\dot{\lambda}$ and its integral $\int_0^{WK} \dot{\lambda} dt = \lambda$ at the WK point, but only weakly dependent on its intermediate values between the shock front and the WK point. These zones of dependency are shown schematically in Figure 11.

8.3.1 X-0219

As a consequence, the CPeX reaction rate surface for X-0219 is very poorly specified, since the WK solution points lie within very tight bands in both pressure and extent of reaction. Indeed, the WK solutions here are more sensitive to the form of the geometrical depletion term, namely $(1 - \lambda)$, than to the characteristic reaction time constants in the reaction rate law. In order to sensibly fix these time constants, it was necessary to supplement the detonation velocity measurements with DYNA2D simulations of the experimental Pop-plot. Thus, only the grey areas in Figure 11(a) are based on experimental data, while the remaining white areas are inferred by extrapolation using the functional forms assumed in the reaction rate law.

Furthermore, after all the calculations reported here had been completed, the papers by Campbell [14]

Figure 11. The areas shaded in grey define where the CPeX reaction rate surface is determined from experimental data. Dark grey signifies a strong sensitivity, while light grey signifies a weak sensitivity, to the data.

and by Chaissé [15] came to our attention, demonstrating that the diameter effect curves for the similar explosives PBX-9502 (95 / 5 TATB / KelF 800) and Composition T (96% TATB) respectively were not linear as previously described by Campbell and Engelke [7] and collated by Gibbs and Popolato [16] for X-0219 and PBX-9502, but instead was concave upwards in large diameter and concave downwards in small diameter. As mentioned in section 4, the chemical equilibrium calculations using IDeX [5] predicted an ideal detonation velocity for X-0219 that was higher than that based on a linear extrapolation of the diameter effect curve. If the diameter effect curve of X-0219 is in fact similar in shape to that of other TATB explosives (and hence incidentally also of HANFO), this would alter the shape of its reaction rate surface in the region $\lambda \approx 0.9$. Rather than the present surface for which $\partial\lambda/\partial\lambda < 0$ and $\partial^2\lambda/\partial\lambda^2 = 0$ in this region, the surface would need to be altered so that $\partial\lambda/\partial\lambda < 0$ and $\partial^2\lambda/\partial\lambda^2 > 0$. This would eliminate all reaction rate laws based on a $(1-\lambda)^n$ depletion term, where $n < 1$ to yield a finite reaction zone length.

Nonetheless, it is believed that the reaction rate surface plotted for X-0219 in Figure 8(a) is realistic away from this region. Sheffield et al. [22] inferred reaction rates in PBX-9502 from subnanosecond resolution particle velocity measurements. They estimated that the initial reaction rate immediately behind the detonation front was $80 \mu\text{s}^{-1}$, and that this rate decreased as the reaction proceeded. This compares favourably with the peak rate of $50 \mu\text{s}^{-1}$ determined here for X-0219, remembering that the failure diameters of these explosives are 9mm for PBX-9502 and 14mm for X-0219.

The only direct experimental estimate of the ZND detonation zone length in X-0219 is 0.3mm from the plate push experiments of Craig (quoted by Campbell and Engelke [7]), based on the break point in a plot of plate velocity versus plate thickness. Measurements on similar TATB-based explosives have given longer values. From their particle velocity experiments, Sheffield et al. [22] estimated that the 1D reaction zone length for PBX-9502 was about 2mm. Davis [23] varied the charge length of PBX-9502 in a plate push experiment, seeking to discriminate between the steady and non-steady flow regimes behind the detonation front — this gave a detonation zone length of 3.3mm. The form of the depletion term, $(1-\lambda)$, adopted in CPeX gives infinite reaction zone lengths in the limit as $\lambda \rightarrow 1$. However, the CPeX detonation zone lengths summarised in Figure 3(f) would support values around 3mm.

8.3.2 HANFO

The diameter effect curve for HANFO covers a broad region of both the pressure and the extent of reaction space, mapping out the surface quite efficiently. Shock initiation experiments are not required in the conventional sense to probe reactivity in the *low* pressure regime. Instead, wedge tests could be used

to probe the *high* pressure regime, where it is not economical to perform detonation experiments. This is the exact opposite of the situation for X-0219.

In particular, the measurements have sampled through the local minimum in the reaction rate surface at $\lambda \approx 0.45$. Such a minimum has not previously been reported in the literature, and indeed, few published reaction rate schemes could accommodate such a minimum.

9. CONCLUDING REMARKS

The behaviour of X-0219 described here exemplifies the type of detonics for which the recent theories by Bdzil et al. [24], by Lambourn and Swift [25], and by Brun [26], have been developed. These theories, which can relate detonation velocity to wavefront curvature in rate stick geometry, all share the common assumption that the thickness of the detonation zone x_{WK} can either be neglected or is much smaller than the other distance scales in the problem (typically either the charge diameter or the shockfront radius of curvature R_s). This is the case for X-0219, where even close to the failure diameter, the ratio $x_{WK} / R_s \approx 0.035$. A short detonation zone necessarily limits the extent of radial divergence that can occur within it, leading directly to 2D detonation in rate stick geometry being only slightly perturbed from 1D detonation in planar geometry. In particular, the pressure, density, and extent of reaction at the WK point of a 2D detonation are all close to their CJ values. X-0219 can rightly be considered an ideal explosive.

This is not true of HANFO, where the differences between the 1D and 2D detonations are profound, and on a scale not previously reported. Here, the ratio $x_{WK} / R_s \approx 0.25$, so that the basic assumption of the wavefront curvature models is violated. The long detonation zones give time for appreciable radial divergence to occur, leading to significant deviations from CJ predictions. Hence, close to the failure diameter, the WK pressure for a 2D detonation is an order of magnitude lower than the CJ pressure of a 1D detonation. HANFO is a highly non-ideal explosive.

This non-ideality derives from the topography of the HANFO reaction rate surface, which in turn derives from the key role that mass diffusion is believed to play in limiting reaction rates in physically heterogeneous explosives. Such non-ideality and heterogeneity challenge both the theoretician and the experimentalist.

The features in the reaction rate surface for X-0219 that make shock initiation a distinct phenomenon from detonation are absent from the surface for HANFO. This must be clearly understood if the hazards of handling highly non-ideal explosives are to be properly assessed.

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