

Full Paper

Small-scale detonation of industrial Urea-Hydrogen Peroxide (UHP)

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Abstract: The adduct of Urea and Hydrogen Peroxide (UHP), also called Carbamide Peroxide, is industrially produced as a solid source of hydrogen peroxide for bleaching, disinfection, and oxidation reactions. As a chemical combination of fuel and oxidiser, UHP has explosive potential but it is unclear whether it could sustain a detonation at small scale. In the configuration we tested, we succeeded in recording self-sustained detonation at relatively small scale under heavy confinement, measuring a maximum experimental velocity of detonation of 3860 m/s at an optimum 1.1 g/cm³ loading density. UHP can sustain a detonation, even at the 100 g scale, but this is strongly dependant on booster size, confinement material, loading density, charge length and diameter. According to our performance assessment, pure UHP exhibits the behaviour of a non-ideal tertiary explosive. Maximum calculated detonation pressures are below 10 GPa, the order of magnitude for commercial blasting explosives. Small-scale results are consistent with literature values from large-scale experiments, although literature on the matter is quite limited. The proposed experimental method can be used to quantify the detonability and performance of other industrial materials that may have energetic properties, or small samples of homemade explosive compositions, avoiding time-consuming, expensive and potentially hazardous large-scale experiments.

Keywords: Urea hydrogen peroxide, Detonation, Non ideal explosive, Performance

1 Introduction

The 2020 Beirut explosion of an estimated 2750 tons of Ammonium Nitrate (AN) was one more tragic illustration of the explosive potential of industrial oxidising chemicals [1-2], which are strictly regulated against illicit use and require specific industrial risk control processes. Hydrogen Peroxide (HP) is another typical example of an oxidiser, widely misused by terrorists over the last 20 years for the synthesis of TATP and HMTD [3-6] or in mixture with organic material (HPOM) [7]. HP can also be explosive on its own at high concentrations [8], which also stimulates current research on novel, green, nitrogen-free, peroxide-based explosives for the mining industry [9-10].

Urea can be directly added to hydrogen peroxide to form an adduct (UHP), which is industrially produced as a solid and stable source of hydrogen peroxide for bleaching, disinfection, and oxidation reactions. As a chemical combination of fuel and oxidiser [11], UHP has explosive potential but the available academic literature about its explosive properties is surprisingly limited.

To the best of our knowledge, the explosive potential of UHP was first reported in 2016 by Hussein [12] and Matyas [13]. Hussein studied the relative explosive strength of mixtures containing urea and/or peroxide, using ballistic mortar techniques and thermochemical calculations. Matyas characterised comprehensively the explosive and thermal properties of UHP. He demonstrated its detonability, recording an experimental velocity of detonation (VoD) of 3778 m/s for a 30 kg charge. However it is unclear whether UHP could sustain a detonation at the 100 g scale.

In this paper, we investigated the detonability of commercial lab grade UHP (97%) at small scale. We studied the effect of parameters such as charge diameter, charge length, loading density and confinement material, together with initiation and boosting material in order to confirm the possibility of detonation at common commercial scales and below, extending previous large-scale publications. Further UHP performance assessment includes witness plate indentation [14-15] and VoD measurements using Optimex 64 [16].

2 Experimental Section

Our methodology (Fig 1) combined theoretical calculation, numerical simulation and a comprehensive experimental campaign, consisting of 40 firings. Theoretical predictions and numerical simulation results were compared with experimental data, obtained at small-scale.

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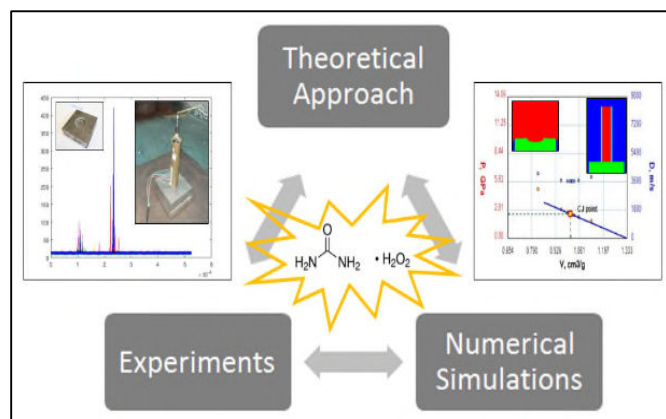


Figure 1. Research methodology.

The experimental approach preceded the numerical approach in order to experimentally validate a set-up that enabled self-sustained detonations to be recorded. This geometry was then numerically simulated in Ansys Autodyn.

We used commercial lab grade UHP (97%) from a single lot purchased from ALFA AESAR – L13940.36. The particle size distribution was determined by dry sieving (Table 1).

Table 1. Particle size distribution.

Mesh size (μm)	Sample retained (%)
1000	15.5
800	41.4
600	28.1
400	14.5
200	0.5

In accordance with Matyas' recommendations regarding thermal stability [13], UHP was stored at 5 °C when not in use and left in ambient conditions for one hour prior to the preparation of each charge.

2.1 Theoretical approach

We used thermodynamic code Explo5 (V6.05) calculations [17] in order to determine the ideal detonation parameters, based on the chemical equilibrium steady state detonation model, and compare them with the values obtained experimentally.

The standard enthalpy of formation of UHP was calculated from calorimetry measurements. A Parr 6200 isoperibol calorimeter (operated under 3 MPa O₂) was calibrated with Benzoic Acid (BA) reference and 10 single measurements were carried out on 1.75 g pellet samples (80% UHP - 20% BA as combustion aid), with no combustion residues observed. The standard enthalpy of formation at 298.15 K was calculated by applying the manufacturer standard methods for thermodynamic calculations.

The theoretically based equation of state (EoS) molecular fluid EXP-6 [18] was selected instead of Becker – Kistiakowski – Wilson (BKW) EoS to give better predictions of detonation velocity and pressure at densities below 1.2 g/cm³. We also used the Explo5

built-in algorithm [19-21] with 2250 K freezing temperature to estimate the Jones-Wilkins-Lee (JWL) coefficients and feed our hydrocode simulation (section 2.3).

2.2 Experiments

2.2.1 Preliminary testing

The objective of the preliminary testing was to define and validate a set-up that enabled self-sustained detonation to be achieved. We used charge masses ranging from 2 g up to 100 g UHP, under light or heavy confinement material, initiated by a pyrotechnical train with or without booster. An overview of the test program is available in Table 2.

Table 2. Preliminary testing.

UHP (g)	ID (mm)	OD (mm)	L (mm)	Confinement	Initiation	# firings
2-5	10	14	50	Steel 316L	Deto N°8	3
100	30	38	150	INOX 321	Deto N°8 + Booster	6
100	30	38	150	PE	Deto N°8 + Booster	3

We selected an initial charge length of 150 mm, corresponding to 5 inner diameters, a commonly used reference for non-ideal commercial blasting explosives [22]. Scaled-up UHP explosive charges (0.75 g/cm³, loose) of approximately 100 g, were initiated with a standard N°8 military detonator and C4 plastic explosive boosters of decreasing size (20 g, 10 g, 5 g, 2.5 g). Explosive charges were initiated in direct contact with a witness plate (Al 6082 T651). The indent depths on the witness plates were measured (0.01 mm accuracy) using a Helios micrometer.

2.2.2 Validated set-up

Anticipating on the results (see section 3.2.1), 100 g UHP charges, confined in steel cylinders of INOX 321, initiated by a standard N°8 military detonator and a 7.5 g C4 booster, were used for further detonation investigations. An overview of the test program is available in Table 3.

Table 3. Validated set-up test program.

	Purpose	# firings
1	Optimum loading density	12
2	Minimum charge length for stationarity	13
3	Velocity of Detonation	15

To optimise the likelihood and reproducibility of the initiation by distributing it over the entire charge diameter, we designed a bespoke conical cup (Fig 2) wherein a booster of constant shape and mass (7.5 g C4) can be moulded and a standard N°8 military detonator can be inserted easily.



Figure 2. 3D printed booster cup.

In order to assess the effect of loading density on detonation parameters, 12 steel cylinders of INOX 321 were loaded at charge densities ranging from 0.75 to 1.45 g/cm³. They were filled stepwise in 4 g increments with UHP to ensure reproducibility and a constant density along the charge. Higher densities were obtained by hydraulically pressing (0.7 to 56 kN). Densities lower than 1 g/cm³ were obtained by vibration, using ballasts on top. Either pressure or vibration was exerted during one minute at each filling step.

The charges were detonated in contact with a 30 mm thick aluminium (6082 T651) witness plate, itself placed on a 20 mm thick anvil, using a standard N°8 military detonator and a 7.5 g C4 booster moulded in a conical cup, producing an initial steady overdriven reaction wave. The indent depth in the witness plate was measured using a micrometer.

As we were detonating UHP charges filled at various densities with all other parameters kept constant (confinement material, length, diameter, orientation, firing set-up and initiator), we investigated the effect of density on the fragmentation pattern using the *Fragment Weight Distribution Map* (FWDM) evaluator [23-24]. This tool has been developed by Oxley to assess the explosive power of pipe bomb devices with a single variable, which is insensitive to percent recovery. Fragments of the steel container (Fig 3) were collected, sorted and weighed according to the described procedure. FWDM slopes were determined and compared to average indent depths on the witness plate as a function of the charge loading density.

In an attempt to assess the minimum charge length to allow self-sustained detonation to develop, 13 additional steel cylinders with lengths ranging from 1 inner diameter (30 mm) to 6 inner diameter (180 mm) were detonated as previously described.

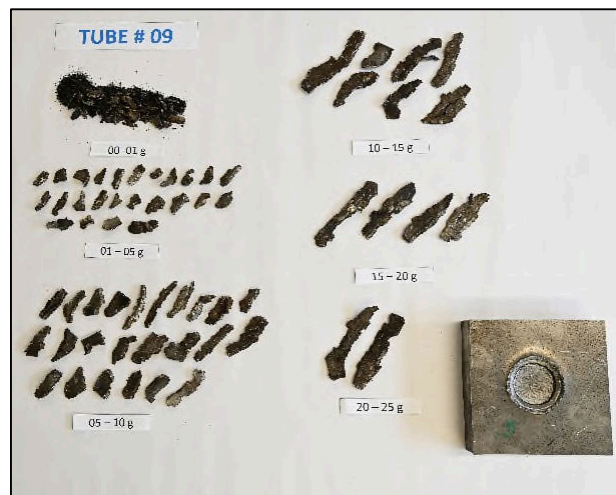


Figure 3. Fragmentation (90% mass recovery) and indent on witness plate for a confined 90 g UHP charge at density 0.83 g/cm³.

Detonation velocities (VoD) were recorded using Optimex 64, the passive optical analyser of explosive processes from OZM Research. We filled 15 additional steel cylinders stepwise at loading densities of 0.75, 1 and 1.1 g/cm³ (accuracy 0.01 g/cm³). The charges were detonated as described previously, with optical probes positioned in accordance with the minimum charge length requirement (Fig 4), after the first 90 mm (3x ID). 8 blind (non through) holes (depth 2 mm; spacing 7.5 mm) were drilled in the lower part of the tube to insert the optical probes safely and accurately, as shown in Figure 5. In this way, the optical probes were protected from noise on the signal and only triggered from the light produced by the adiabatic compression of the air trapped in the blind hole as the detonation front passed. The VoD is calculated from the recorded arrival times and the known distance between probes.

The detonation pressure can be calculated at different loading densities ρ_0 , using [25]:

$$P_{det} = \frac{\rho_0 \cdot (VoD)^2}{\gamma + 1} \quad (1)$$

A good estimate of the detonation pressure of typical military explosives with densities ranging from 1 to 1.8 g/cm³ can be obtained using a ratio of the specific heats of the detonation product gases equal to 3. However, this value is overestimated for non-ideal explosives with lower detonation velocities, such as AN-based explosives. Detonation pressure was hence calculated from Cooper generic experimental correlation, which covers a wider range of densities:

$$P_{det} = \rho_0 \cdot (VoD)^2 \cdot (1 - 0,7125 \cdot \rho_0^{0,04}) \quad (2)$$

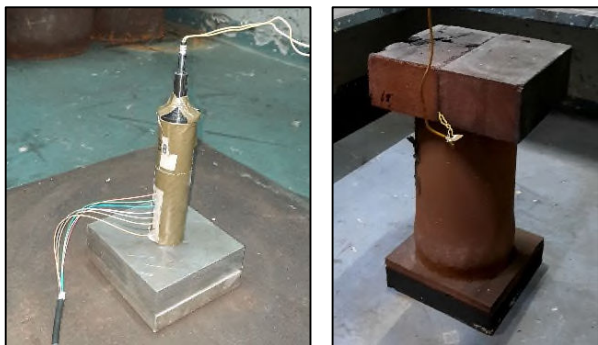


Figure 4. Set-up for detonation of confined UHP charge with vertical initiation, witness plate, anvil, optical probes (left), protective structure to optimise fragment recovery (right).

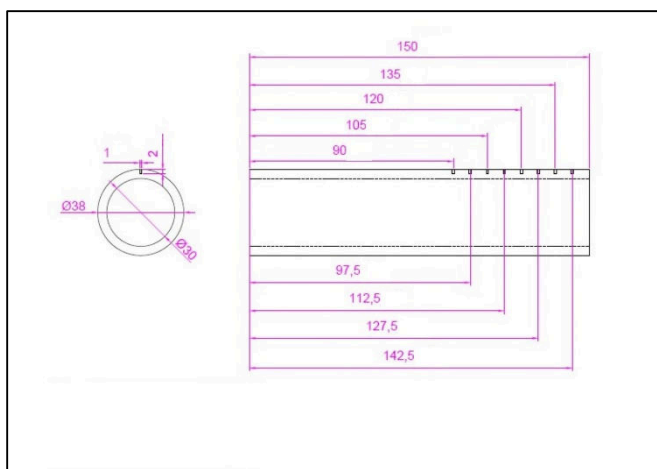


Figure 5. Blind holes in steel container for optical probes positioning (all dimensions in mm, tolerance 0.01 mm).

2.2.3 Experimental results assessment

We used the following data to assess UHP detonation performance:

- Visual observation and measurement of the indent depth on the witness plate.
- Visual observation of the fragmentation pattern and calculation of the FWDM slope.
- Measurement of detonation velocities.
- Calculation of detonation pressure.

This enabled us to derive a correlation between detonation pressure and indent depth.

2.3 Numerical approach

The ultimate aim of the numerical approach is to model UHP detonation prior to further large-scale experiments and risk assessment analysis. Within the scope of this paper, we simulated the set-up in Ansys Autodyn V14.0 in order to model the indentation on the witness plate and compare it to experimental values. As UHP was not

available in the Autodyn library, it was defined using the Chapman-Jouguet (CJ) state ideal parameters and theoretical JWL coefficients estimated from Explo5 calculations (section 2.1). Geometry was chosen as 2D, axisymmetric with mesh size 0.5mm. We used EULER type interactions to overcome interfaces problems and two boundary conditions to fix the bottom of the witness plate (*fix*) and to allow detonation gas to escape through the top of the tube (*flowout*).

3 Results and Discussion

3.1 Theoretical approach

The detonation parameters from the Explo5 calculations, based on a standard enthalpy of formation of -563 kJ/mol calculated from calorimeter results, are available in Table 4. The use of EXP-6 EoS enabled us to estimate JWL coefficients along the detonation products isentrope for explosives with low detonation temperature, when pressure quickly drops to atmospheric.

Table 4. Theoretical detonation parameters (CJ point).

Loading Density (g/cm ³)	0.75	0.9	1	1.1
Heat of Detonation (kJ/kg)	-2447	-2496	-2564	-2621
Detonation Pressure (GPa)	2.42	3.86	5.48	6.92
Detonation Velocity (m/s)	3657	4339	4774	5215

These values are theoretical maximum, assuming ideal detonation and infinite charge diameter, with no account of confinement, grain size or critical diameter. We used these maximum values to estimate the theoretical TNT equivalence and dimension our charges according to our firing bunker NEQ limitations, obtaining respectively 0.8 (power index) and 0.5 (hydrodynamic work) [26].

3.2 Experiments

3.2.1 Preliminary testing

In our set-up, UHP charges (2-5 g) directly initiated by a standard N°8 military detonator failed to detonate, even under heavy confinement. Only combustion was observed, with no detonative output. These experiments did not provide any further technical information but increased our confidence to scale up UHP charges. A minimum booster charge of 5 g C4 was necessary to initiate UHP explosive charges of approximately 100 g confined in steel cylinders. However, we scaled it up to 7.5 g to avoid geometrical effects and distribute the initiation over the entire charge diameter, using a bespoke booster cup. 100 g UHP charges confined in thick polyethylene cylinders initiated by a standard N°8 military detonator and a 7.5 g C4 booster failed to sustain detonation (Fig 6). The

upper part of the PE tube was shattered due to the detonation of the C4 booster. The UHP charge could not further sustain the detonation in a light confinement material such as plastic. A heavy confinement is required to achieve self-sustained detonation in UHP. This is consistent with literature [13] where failed detonation and explosion decay have been observed for similar UHP charges under intermediate confinement (copper, ID 36 mm).



Figure 6. Light confinement – failed detonation: absence of indentation in the plate, presence of unreacted UHP and fragmentation pattern, including petalling of the bottom of the tube.

Scaled-up charges of around 100 g UHP, confined in steel cylinders of INOX 321, initiated by a standard N°8 military detonator and a 7.5 g C4 booster, sustained detonation with indent depth around 5 mm in the witness plate (Fig 7). This latter set-up was validated and selected for further experiment and modelling.

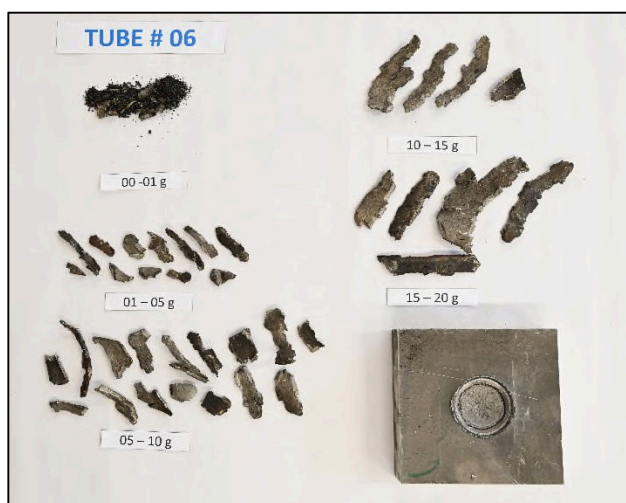


Figure 7. Small-scale detonation of UHP under heavy confinement.

3.2.2 Validated set-up

The effect of UHP loading density was first investigated, using our validated set-up. The average measured indent depth increases almost linearly with growing loading densities, between 0.75 g/cm³ (loose) and 1.1 g/cm³ (pressed), as illustrated in Figure 8. Indentation then drops rapidly and less reproducible responses are observed in the interval 1.1-1.2 g/cm³. This is probably explained by a decrease in shock sensitivity of pressed UHP due to pressurisation, which decreases the density of potential hotspots that play a key role in detonation propagation in heterogeneous explosives [15, 27].

Evidence of deflagration is recorded in the density range of 1.2 -1.3 g/cm³ (Fig 9). In our charge diameter, confinement and initiation conditions (C4 booster incident steady detonation), indications of dead-pressing are observed at densities above 1.3 g/cm³, including further compaction of the UHP by the shock wave, with spalling in the charge at the back of the tube, absence of fragmentation and limited dispersal of unreacted UHP. Further investigations would be necessary to statistically study UHP dead-pressing density and dying-out distance [28]. In our set-up geometry, we could not record sustained detonations at densities closer to 1.43 g/cm³ TMD [13], and maximum performance was observed at a density of 1.1 g/cm³, which we further used for theoretical predictions and modelling.

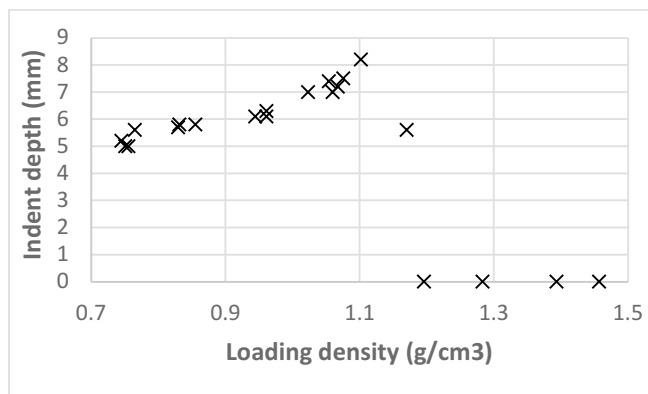


Figure 8. Indentation of witness plate as a function of loading densities for charge lengths equal to 5 x ID.

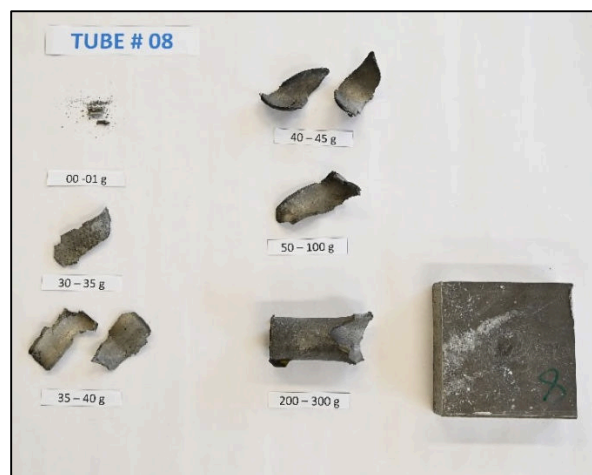


Figure 9. Typical deflagration fragmentation pattern (98% recovery), observed at densities above 1.2 g/cm^3 with a small number of large, bent and torn fragments, with 90° fracture edges.

A good correlation was found between the indentation of the witness plates and the slopes of the FWDM plots. Both parameters are deemed complementary to assess the brisance of a confined explosive charge, i.e. its destructive fragmentation effect on its immediate vicinity [29]. As expected, the brisance increases at higher densities, with maximum FWDM slope and indent depth at 1.1 g/cm^3 density (Fig 10), while deflagrations are recorded at densities above 1.2 g/cm^3 .

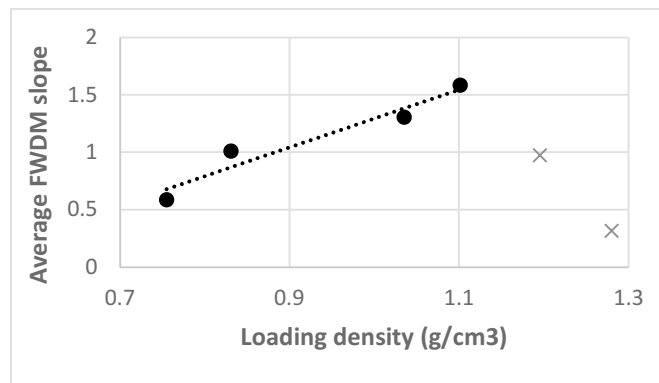


Figure 10. Maximum FWDM slope calculated at a density of 1.1 g/cm^3 . Difference between detonations (black) and deflagrations (grey) are highlighted.

In the configuration we tested and depending on loading density, stationarity is already observed at charge lengths ranging from 2 to 3 inner diameters as shown in Figure 11.

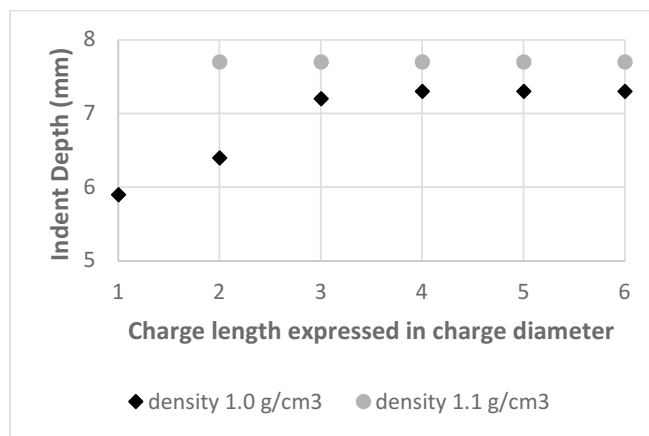


Figure 11. Indentation as a function of charge length.

The experimental VoD values (Table 5) are only about 80% of the CJ ideal theoretical predictions from Explo5. On the one hand, this could suggest that side effects affect the VoD value and that higher VoD could be recorded at higher charge diameter for a given loading density [30]. On the other hand, non-ideal behaviour can also be intrinsic and our experimental values could be close to the maximum achievable VoD for UHP. These questions could be answered by carrying out a comprehensive large-scale parametric study focused on the influence of density, diameter and confinement. However the consistency of our small-scale results with literature values from large-scale experiments [13] shows that our study efficiently reflects the detonation property of UHP, allowing lab-scale studies to be performed.

3.2.3 Experimental result assessment

An overview of the performance parameters of UHP is available in Table 5. We derived an experimental linear correlation between the calculated detonation pressure and measured indent depth. This correlation was further compared to ideal values obtained from Explo5 and Autodyn simulation (section 3.3). Figure 12 further compares witness plate indentation for different UHP loading densities.

Table 5. Performances of UHP charges ($L = 5 \times ID$).

Loading Density (g/cm^3)	0.75	0.9	1	1.1
Average Indent depth (mm)	5.1	6.2	7.1	7.8
Average FWDM slope	0.59	/	1.30	1.58
Average VoD (m/s)	2897	<u>3517</u> ^a	3647	3860
Calculated P_{det} (GPa)	1.86	3.06	3.82	4.67

^a : value taken from Matyas [13], VoD for a 8 kg UHP charge confined in a 8 mm thick steel container ($ID = 124 \text{ mm}$)

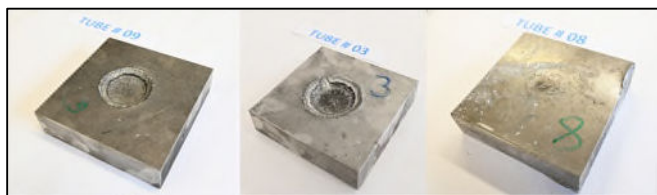


Figure 12. Detonation and indentation at respectively 0.75 g/cm³ (left), 1.1 g/cm³ (middle). Deflagration with no indentation at 1.2 g/cm³ (right).

3.3 Numerical approach

Table 6 gives an overview of the UHP JWL coefficients from Explo5 [17], required to feed the numerical modelling. Indentations on the witness plate are summarised in Table 7 and pictured in Figure 13.

Table 6. JWL coefficients (Explo5).

Loading Density (g/cm ³)	0.75	0.9	1.1
A (GPa)	102.8273	203.2893	470.6499
B (GPa)	1.4169	2.5687	5.5299
R1	5.5826	5.6525	5.921
R2	1.4846	1.5474	1.7225
w	0.3102	0.3081	0.3001

Table 7. Indentation values from numerical simulation.

Loading Density (g/cm ³)	0.75	0.9	1.1
Indentation (mm)	5.5	7.0	9.5

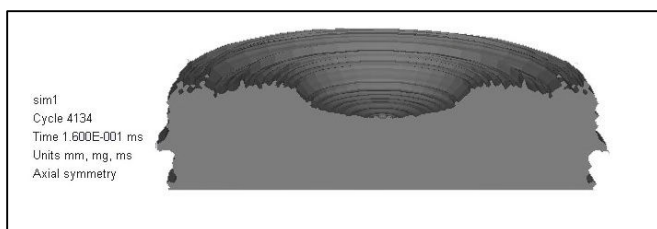


Figure 13. 2DE simulation – indentation witness plate

We previously derived an experimental linear correlation between the calculated detonation pressure and measured indent depth. This correlation is here further compared to ideal values, obtained from Explo5 and Autodyn simulation (Fig 14). Even if they are within the same order of magnitude, the experimental detonation pressure is up to 33% lower and the resulting indentation of the witness plate up to 20% lower than the simulated ones, especially at growing densities. This can be explained by the fact that our numerical model was fed with theoretically ideal performance parameters, i.e. detonation velocity and pressure.

However, both correlations are in good agreement, suggesting that a ratio of the specific heats of the detonation product gases equal to 2.5 is more suitable to estimate the detonation pressure of UHP charges.

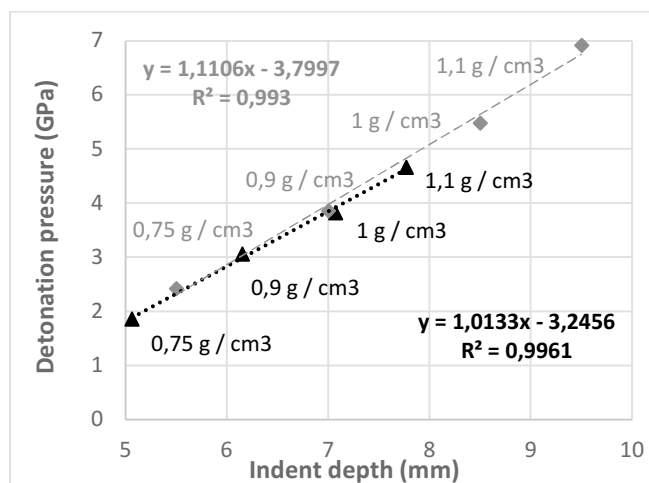


Figure 14. Experimental (black) and simulated (grey) linear correlations between detonation pressure and indent depths.

Our model used Chapman-Jouguet state ideal parameters from Explo5, making it more suitable for conventional explosives [15]. We may speculate that the use of reactive flow models to simulate the detonation behavior of confined non-ideal explosives would better match experimental data [31]. However, current UHP characterization in Autodyn is deemed satisfactory and will be further used to model future larger-scale experiment, including underwater firings.

4 Conclusion

In this paper, we have shown that commercial lab grade UHP (97%) is detonable at small scale. We studied the effect of initiation, charge length, charge diameter, confinement material and loading density and validated a geometry and a bespoke pyrotechnical train. In this configuration, we succeeded in accurately recording self-sustained detonation at relatively small scale under heavy confinement. Optimex 64 has proven reliable for lab-scale VoD measurements, even for non-ideal explosives. Our small-scale results are consistent with literature VoD values from large-scale experiments.

Maximum detonation performances were measured at an optimum 1.1 g/cm³ loading density. In our set-up, deflagration or dead-pressing are observed at higher loading densities. Maximum calculated detonation pressures are below 10 GPa, the order of magnitude for commercial blasting explosives. To estimate the detonation pressure of UHP charges, a value of 2.5 for the ratio of the specific heats of the detonation product gases was found more suitable.

Our numerical model, including UHP characterization with JWL coefficients from Explo5 built-in algorithm was deemed satisfactory and will be further used to model future larger-scale experiment, including underwater firings, and related risk assessment analysis.

The proposed experimental method can be used to quantify the detonability and performance of other industrial materials that may have energetic properties, or small samples of homemade explosive compositions, avoiding time-consuming, expensive and potentially hazardous large-scale experiments.

Symbols and Abbreviations

AN	Ammonium Nitrate
BA	Benzoic Acid
BKW	Becker Kistiakowski Wilson
CJ	Chapman-Jouguet
EoS	Equation of State
FWDM	Fragment Weight Distribution Map
HMTD	Hexamethylene Triperoxide Diamine
HP	Hydrogen Peroxide
HPOM	Hydrogen Peroxide Organic Material
ID	Inner Diameter
JWL	Jones Wilkins Lee
L	Charge Length
NEQ	Net Explosive Quantity
OD	Outer Diameter
PE	Polyethylene
TATP	Triacetone Triperoxide
TMD	Theoretical Maximum Density
TNT	Trinitrotoluene
UHP	Urea Hydrogen Peroxide
VoD	Velocity of Detonation

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