



Detonation Characteristics of a NO_x-Free Mining Explosive Based on Sensitised Mixtures of Low Concentration Hydrogen Peroxide and Fuel

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Abstract: Mining explosives based on ammonium nitrate(V) are safe and effective, however, the risk of NO_x fume production during blasting is still present. In 2013, a project to eliminate NO_x fumes from blasting began and hydrogen peroxide was chosen to replace ammonium nitrate(V) as the oxidiser. Previous work in this area demonstrated that hydrogen peroxide/fuel-based mixtures were able to detonate, provided that they are initiated under a situation of high confinement and also using hydrogen peroxide at relatively high concentrations. In contrast, a comprehensive study was conducted to determine the detonation properties of hydrogen peroxide/fuel-based mixtures that used hydrogen peroxide at lower concentrations (below 50 wt.%), detonated in unconfined conditions and used void sensitisation to achieve an efficient detonation reaction. This article presents the results of the influence of the density, water content, critical diameter and type of void sensitisation on the velocity of detonation (VOD) of hydrogen peroxide/fuel-based explosive mixtures. The results indicate that the mixtures can achieve a different VOD which depends on the size of the sensitising voids and more importantly, the mixtures behave as non-ideal explosive, similarly to ammonium nitrate-based explosives, but with the advantage of being a NO_x-free explosive.

Keywords: hydrogen peroxide, NO_x free mining explosives, detonation, hot spots

1 Introduction

Currently most of the commercial explosives used in mining and civil blasting applications are based on mixtures of ammonium nitrate(V) (AN) with fuel.

These mixtures are commonly known as ammonium nitrate(V)/fuel oil (ANFO), emulsion and watergel explosives. Literature describing formulations, detonation properties, applications, *etc.* is given elsewhere [1-5].

Despite being safe and excellent explosives, one of the disadvantages of AN-based explosives is that they may produce NO_x fumes from inefficient reactions caused by the complex interaction of unpredictable ground conditions and/or poor implementation practices. These fumes can cause health issues and in some countries, government regulators have intervened in the matter. The evolution of NO_x fumes has been investigated by various researchers in the past [6, 7]. Additionally, documents addressing the management of NO_x fumes before and after blasting have been issued by government regulators and industry in Australia [8, 9]. To address this problem, work was undertaken to find potential oxidiser materials that could substitute the AN present in current mining explosives, and thus truly eliminate the chances of producing NO_x fumes. In order to achieve this objective, the potential AN replacements should have no nitrogen in the molecule and be mass produced. One of these potential substitutes is hydrogen peroxide (HP). This material is an oxidiser, mass manufactured, which has shown in past studies that when mixed with fuel, it can detonate under certain conditions of high concentrations and confinement [10-12]. However, those detonation studies of HP/fuel-based mixture did not consider relatively low HP concentrations (*i.e.* 40 wt.% -50 wt.%) with void sensitisation.

Although mixtures made with low concentration of HP would be insensitive to initiation, void sensitisation can confer sensitivity of the mixtures. Void sensitisation is a standard process used with AN-based mining explosives and the process is applied at the point of loading (which increases the safety when handling, transporting, storing and using mining explosives).

Detonation tests were conducted using lower HP concentration and sensitising methods to determine if mixtures were able to detonate. Results of these detonation tests were published in 2013 [13, 14] and studied the influence of both density and the diameter of the charge on the VOD. That study revealed that HP/fuel-based mixtures were able to detonate when sensitised with glass microballoons (GMB) and more importantly, that HP/fuel-based explosives, similarly to AN-based explosives, belong to the group II of explosives, where VOD depends on the density, as defined by Price [15].

Due to the success of this early study, more comprehensive work was conducted to determine the influence of variables such as density, type of sensitisation, water content and combination thereof on the VOD of HP/fuel-based mixtures. Results from these are discussed in this article.

2 Experimental section

2.1 Formula

Table 1 displays the formula studied in this work. HP/fuel-based mixtures were prepared with HP 35 wt.%, 40 wt.% and 50 wt.%. As fuel, a mixture made up of glycerine and xanthan gum was used. The fuel phase content varied between 14.0 wt.% - 17.0 wt.%. The total water content varied between 41.5 wt.% and 56.6 wt.%.

Table 1. Formulas tested

HP concentration [wt.%]	35	40	50
Component			
HP [wt.%]	30.45	34.40	41.50
Water [wt.%]	56.55	51.60	41.50
Fuel [wt.%]	13.00	14.00	17.00
Density [g/mL]	1.14	1.16	1.20
OB	-1.04	-0.42	-0.56

The types of sensitising voids used in this study were:

- GMB Q-cel 5020, not sieved, with a particle size of 20-120 μm ;
- chemical gas bubbles, with a particle size of 100-400 μm ;
- Expanded polystyrene (EPS) voids, with a particle size of 5500-7500 microns.

The sensitising voids were hand-mixed into the HP/fuel-based mixtures using a plastic spatula and a 5-Litre plastic container. In this way the potential of any friction event that could initiate the explosive was lowered. In order to chemically gas the mixtures, a solution of NaOH (13.0 g/L) and NaHClO (52.5 g/L) was used to decompose the hydrogen peroxide and produce gas bubbles. The amount of HP decomposed for gassing was minimal and did not affect the total strength of the HP as oxidiser in the oxidiser solution.

The lowest density achieved when using GMB for sensitisation was 0.75 g/mL. At this density, due to the GMB load, the mixtures become too thick and there was too much friction when mixing. For safety reason no more incorporation of GMB was tried.

EPS was sourced from the supermarket and then sieved.

2.2 Detonation tests

The HP/fuel-based mixtures were loaded into PVC tubes (mostly 102 mm inner diameter, 1 mm wall thickness and 600 mm in length). The charges were initiated with a 50 g pentolite booster. Conical charges were also used to determine

critical diameter. Pipes/cones with the explosive were loaded and fired the same day. A small 25-gram booster and an electric detonator were used to initiate the charges. The VOD was continuously measured using the MREL-Microtrap data acquisition system. The VOD cable was externally attached to the PVC pipe.

3 Results and Discussion

3.1 Range of formulas tested

Previous work by Shanley *et al.* [10] showed that HP/fuel mixtures (where acetone, ethanol, glycerine, *etc.* were used as fuel) were able to detonate in a wide range of proportions under confined conditions and no sensitisation. Most of the mixtures are inefficient from a mining application perspective as they were not oxygen balanced. More specifically one of the components of the mixture is in excess (either oxidiser or fuel) and this excess will not react during the detonation process and therefore will not contribute to the release energy to sustain the detonation. This excess will only absorb energy and hence their unsuitability for practical blasting applications. Excess fuel will also produce unwanted reaction by-products (CO).

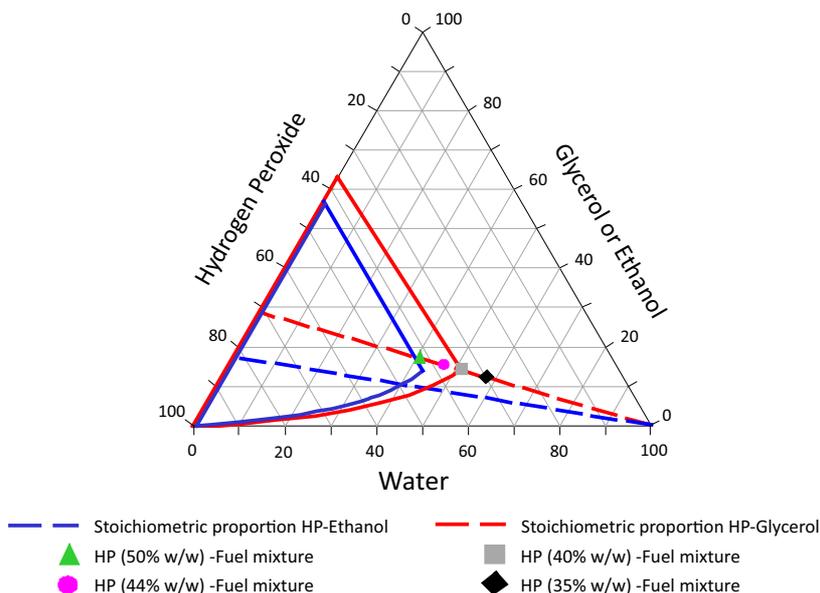


Figure 1. Ternary diagram displaying the detonation ranges of HP/fuel mixture according to Shanley *et al.* The plot also displays the formulas investigated in this research

In this work, only HP/fuel-based mixtures that were oxygen balanced were studied. These compositions are displayed in the ternary diagram in Figure 1 (along the dotted red line, which correspond to the HP/glycerol mixtures).

The HP/fuel-based mixtures were sensitised by incorporating physical voids (GMB or EPS) or by generating *in-situ* bubbles (chemical gassing). The incorporation of the sensitising voids caused, of course, a drop in the density of the HP/fuel-based mixtures.

3.2 Thermodynamic calculations

It is observed that formula prepared with 50 wt.% of HP has an energy of 4.66 MJ/kg. This energy is higher than ANFO, which is 3.60 MJ/kg. The other two formulations have a lower energetic content than ANFO (2.90 MJ/kg and 3.48 MJ/kg for 35 wt.% and 40 wt.% respectively). Plots from the thermodynamic calculations for the HP/fuel-based mixtures prepared with HP of different strength (40 wt.% and 50 wt.%) are presented in Figure 2. The plots show both the ideal VOD and ideal detonation pressure) when using different sensitisation.

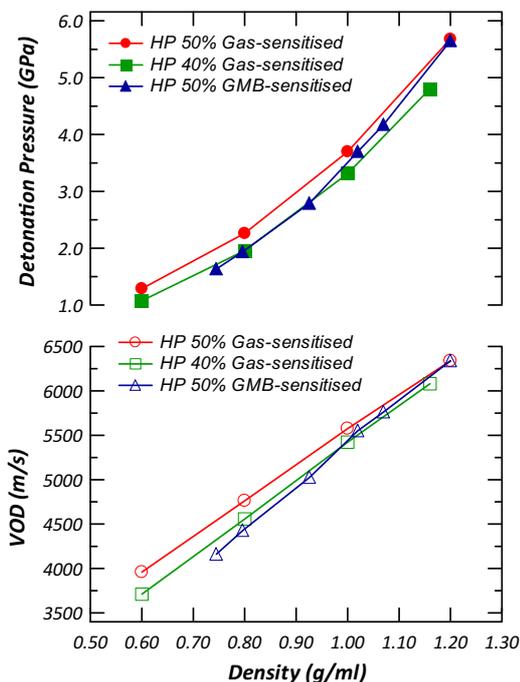


Figure 2. Thermodynamic calculations of HP/fuel-based mixtures, with different densities, sensitisation type and water content

The thermodynamics properties were calculated using an ideal detonation code. It is seen that the VOD and detonation pressure drops with the density. It is also interesting to see that there is not significant difference in VOD or detonation pressure between samples made with HP 50 wt.% or HP 40 wt.%.

3.3 Influence of the type and size of the void on the detonation properties

The relationship between the density of the HP/fuel-based mixture (in the range 0.30 g/mL - 1.2 g/mL and prepared with HP 50 wt.%) and the VOD, when using different void size, is displayed in Figure 3.

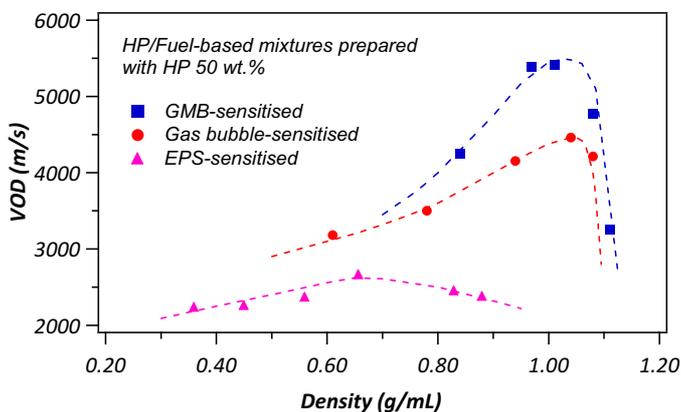


Figure 3. Relationship between density and VOD, using different sensitising voids

It has been noted that the VOD of the HP/fuel-based mixtures drops considerably in the density range 0.3 g/mL - 1.00 g/mL when EPS is used as sensitising voids. This behaviour has also been found in previous work [16], however no hypothesis was presented to explain the mechanism by which the VOD drops when using large voids for sensitisation.

The shape of the Density Vs VOD curve shown in Figure 3, which shows a peak on the VOD, is characteristic of an explosive from Group II [15]. However, a few interesting features are seen when the size of the void increases. Firstly, the VOD peak for the GMB-sensitised mixture is at a density of around 1.00 g/mL versus 0.65 g/mL, when compared to the EPS-sensitised mixture. This shift of the VOD peak of the mixtures towards higher densities when the sensitisation void's size decreases is in line with previous published results [17, 18]. Secondly, for the same product, different densities could achieve the same VOD. For example,

the gas-sensitised products (at density of 0.90 g/mL or density 1.04 g/mL) can achieve VODs of approximately 4000 m/s. However, the product at density 0.90 g/mL has between 2-3 times as much GMB (by volume) than the product at density 1.04 g/mL. This high amount of GMB is diluting the HP/Fuel-based mixture (less energy release per unit of volume) which causes a low VOD and in turn a lower detonation pressure. This would also translate into a different blasting result at a mine scale.

We also hypothesized that there are two factors to consider in the decomposition and ignition of the energetic material along the VOD curve:

- heat produced by the hot spot;
- heat released by the shocked and ignited material.

In the high density of the curve, hot spots decompose the material they are in contact with but after that, the heat released by the decomposed material is the main factor to continue the ignition and sustain the detonating process. However, at low densities (left hand side of the VOD curve), the amount of heat released is quite low mainly due to the low amount of energetic material being shocked and decomposed. The heat released may not be sufficient to decompose and ignite the unreacted material to continue sustaining the detonation reaction. Therefore, hot spots, which are abundant in the low density section, are the main factor that influences the ignition of the energetic material.

Regarding the void size influence on the VOD, a picture showing the size for both EPS and GMB is displayed in Figure 4. The distribution size is also shown [19].

It can be observed that the size distributions for EPS and GMB differ greatly. The size distribution of gas bubbles is slightly higher than GMB ones, so it will not be included in this comparison.

The drop in the VOD of the EPS sensitised mixtures might depend on both the large size of the voids and the area of the HP/fuel-based mixtures that is exposed to the voids.

The area of the HP/fuel-based mixtures exposed to the GMB voids is around 120-130 times larger than the area exposed when using EPS. This exposed area difference and the high number of hot spots generated when the shock wave passes, may be the cause of the high VOD for GMB sensitised mixtures. To explain the low VOD, in a wide range of densities for the EPS sensitised mixtures, is a more difficult task. The number of hot spots is very low, and so is the surface area exposed to the voids but the HP/fuel-based mixtures still detonate.

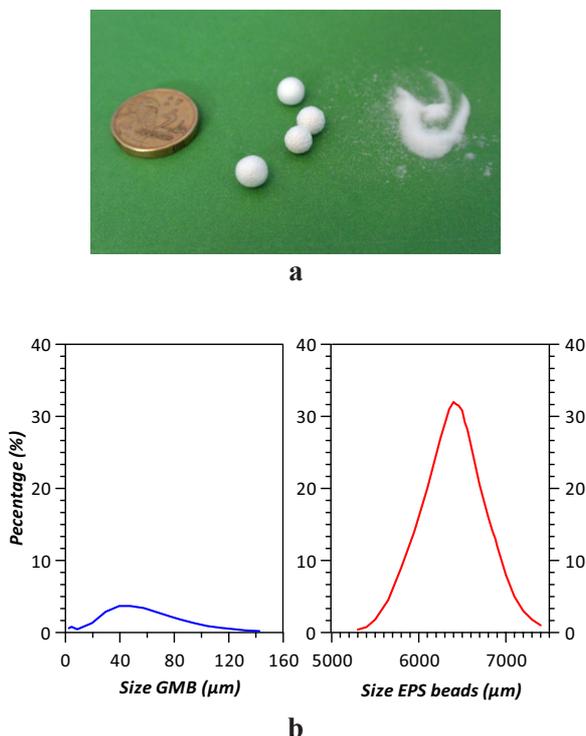


Figure 4. Pictures of EPS (middle) and GMB (a). The coin at the left hand side is 20.5 mm in diameter. The plots for the distribution size are also shown (b)

It is postulated that other detonation mechanisms are manifested when EPS (or, in general, large sensitising voids) is used. For example, Field suggested that for large cavities, void collapse is relatively slow and adiabatic heating of the gas is important. However, if very high shock pressures are involved, then the “hot spot” produced by jet impact could be significant [20]. Mader also suggested this jet impact mechanism for the decomposition of energetic materials [21, 22]. In this case, the shock pressure for the EPS-sensitised HP/fuel-based mixtures may be between 1-3 GPa (according to Figure 2), which would fit with Field’s and Mader’s theory. It is believed that the time taken for the EPS voids to collapse could be longer than the time for the formed jet to hit the material and start decomposing it by friction or any other mechanism. Thus, jet impact is the predominant factor rather than adiabatic heating in the low density section when using large voids.

Another interesting theory has been given by Menikoff’s simulation [23].

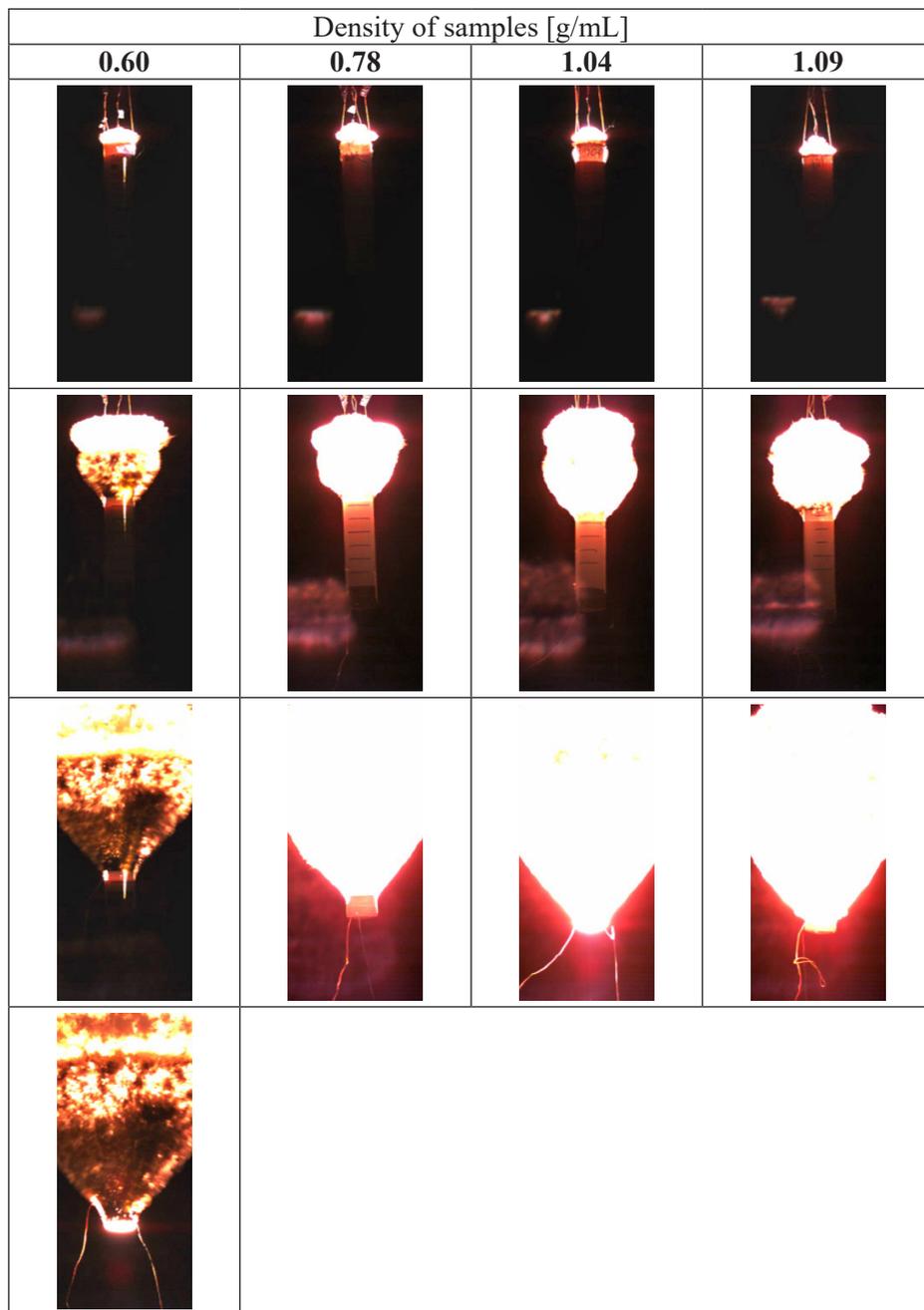


Figure 5. High speed video of the detonation of gas bubble-sensitised HP/fuel-based mixtures

When the shock wave passes through the large voids, the jet starts forming, but at the same time, and a lot faster, the shock waves start bouncing back at the other side of the voids. This causes further interaction between the multiple shock waves bouncing which assist with the explosive decomposition. These collisions of bouncing shock waves might not happen when the voids are smaller like GMB or chemical gassing bubbles.

For smaller cavities down to 1-micron diameter, viscous and plastic heating mechanisms dominate [24], however in the current study that small size of void was not used. Finally, the mixtures, especially those sensitised with EPS, are far from the ideal VOD.

3.4 High speed video footage

High speed video footage (90,000 frames per second) was taken from the detonation process of the HP/fuel-based mixtures sensitised with gas bubbles and detonated in 102 mm diameter PVC pipes. Figure 5 displays still pictures taken from the high speed video. Points at densities 0.60 g/mL, 0.78 g/mL, 1.04 g/mL and 1.09 g/mL are shown. The individual frames are at 11 μ s, 55 μ s, 132 μ s and 176 μ s (only for density 0.60 g/mL).

The VOD obtained from the still frames match the VOD measured with the VOD instrument. It was observed that for density 0.60 g/mL, the expanding gases show a different color if compared with high densities' gases. This is likely to be related to the temperature generated by the detonation process. From the still images, the length of a "reaction region", for the product at density 0.60 g/mL, can be calculated. Each mark in the pipe is 50 mm apart, hence a rough calculation shows that the length of this "reaction region" is around 30 mm. This appears to be at least 300 times longer than the reaction zone of high explosives such as PBX 9494 or composition B, which shows reaction zones of about 0.01-0.1 mm [25]. From the footage it was also seen that for different densities the expanding gases form a slightly different angle with the side of the pipe; and that the reaction regions appear to be different. Further analysis is being conducted to determine the causes for these differences.

3.5 Water content influence on the VOD

Figure 6 displays the VOD results of the HP/fuel-based mixtures when the water content of the formula was increased by using HP 40 wt.% instead of HP 50 wt.%. As expected, the increase of the water content decreases the VOD of the product in the density range of 0.80-1.10 g/mL.

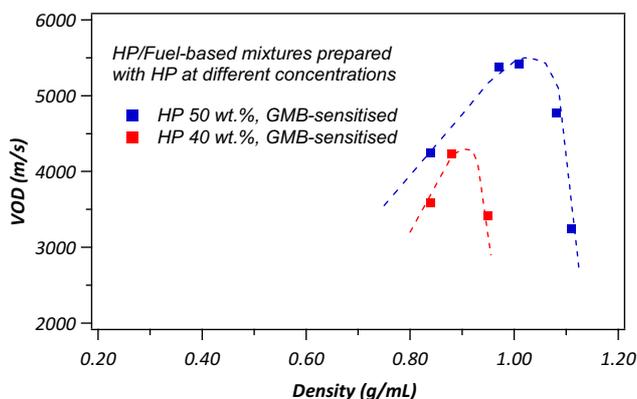


Figure 6. Relationship density vs VOD at different water contents

It was also found that the HP/fuel-based mixture made with HP 35 wt.% did not detonate in 102 mm, neither at densities of 0.55 g/mL nor at 0.90 g/mL (using gas bubbles and GMB sensitisation respectively). It was surprising to find that the HP/fuel-based mixtures (prepared with HP 40 wt.%) with a total water content of 51.6 wt.% were able to detonate. However, the detonation's density range for product is narrower – between 0.80 g/mL and 1.00 g/mL.

It is assumed that if the water content keeps increasing, the VOD will tend to decrease and the detonation range will become narrower, until the product detonates at only one density (for a determined diameter) and that density will be characteristic for that composition.

If the results of this study are compared with those obtained for ANFO or for emulsions, it is observed that HP/Fuel-based mixtures are able to detonate with a larger load of water. Yancik found that ANFO start failing to detonate when the water content reached 9 wt.% [3]. In the case of emulsions, there is evidence at laboratory scale that they start failing at about 35 wt.% [26] and 33 wt.% [27] water content. The reasons the increase of water renders the HP/fuel-based mixture (or any explosive) insensitive are:

- the heat of reaction released by volume of explosives decreases; and this low amount is unable to sustain the decomposition process, therefore the VOD drops or the mixture becomes more insensitive [28];
- water absorbs heat to become steam during the detonation process but steam does not participate in any reaction and therefore does not release any heat.

3.6 Critical diameter

Conical charges were detonated to determine the critical diameters [29] of the HP mixtures made with HP 50 wt.%. Figure 7 shows the residues of the tests. Note that a full cone is shown at the right hand side of the picture.

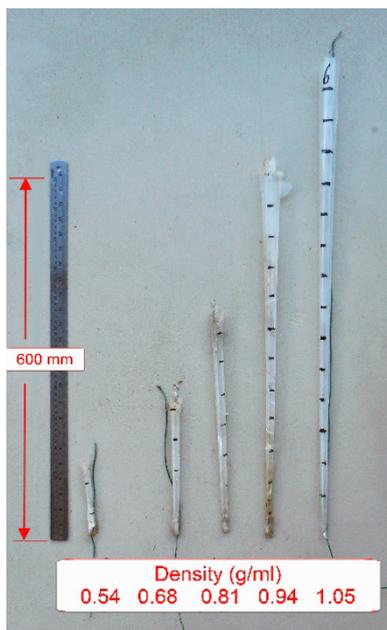


Figure 7. Remnants of the conical charges

No remnants of the conical charge were found for the HP/fuel-based mixture at density 0.68 g/mL. At this stage it is assumed that the product fully detonates and the critical diameter for that density would be below 8 mm. Table 2 displays the critical diameter at which the detonation stopped with the VOD at that diameter (note that more tests are needed to determine the exact VOD).

Table 2. Critical diameter of samples and VOD at that diameter

Density [g/mL]	Critical diameter [mm]	VOD at critical diameter [m/s]
0.54	13±2	1916
0.68	<8	2477
0.81	1 ±2	2161
0.94	20±2	1777
1.05	>34	1725

Results showed that the lower the density, the smaller the diameter at which the product detonates. However, below certain densities, the critical diameter starts increasing. Figure 8 displays the critical diameter and VOD plot for the conical charges.

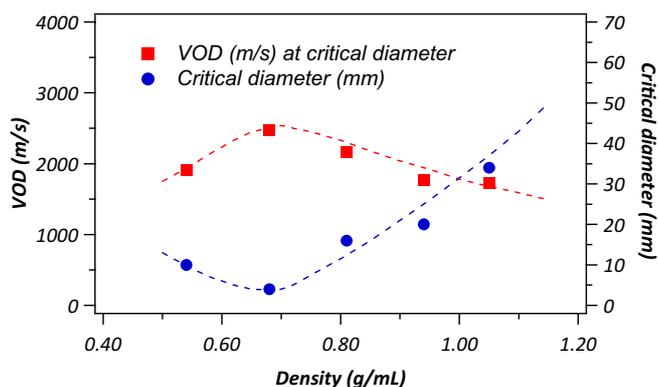


Figure 8. Plot density vs. VOD at critical diameter and critical diameter of the samples

From these results it is inferred that there is a change in the behaviour of the HP/fuel-based mixtures at low density. According to Price [15] the difference between Group I and Group II explosives is that high explosives (Group I) increase their critical diameter when voids are incorporated (which also brings the density down). Group II explosives on the contrary, the critical diameter decreases when voids are incorporated. However, Price also acknowledges that in some explosives there is a transition zone. In this case, at density below 0.60-0.65 g/mL, the HP/fuel-based mixtures seem to behave like explosive Group I – the critical diameter starts increasing with an increase in the volume of voids. The results from this cone experiment show that sensitivity and high VOD of detonation are not correlated. It seems that the more voids are present in the HP/fuel-based mixtures, the higher the sensitivity of the HP/fuel-based mixtures, but this does not translate into a higher VOD.

4 Conclusions

The detonation properties of new explosive products based on HP/fuel-based mixtures have been determined. In the past, studies on the detonation of HP/fuel-based mixtures have been conducted, but in this study, the mixtures

were sensitised with voids. But more importantly, the concentrations of the HP solutions to prepare the HP/fuel-based mixtures were lower than in those previous studies.

It was observed that on the high density side, both the VOD and shock pressure are high, but beyond higher densities, despite the high shock pressure, the detonation fails catastrophically because the hot spots fail to decompose enough material to sustain the detonation process.

On the other hand, it is hypothesized that for mixtures with a high percentage of voids (lower densities), the mechanism of initiation is different to the mechanism when the void presence is lower (higher densities). The large amount of voids that is present at lower densities provides most of the heat needed to decompose the energetic material. The energetic material being decomposed also assists in decomposing undetonated material, but to a lesser degree.

The HP/fuel-based mixtures are able to detonate at high water content. Most probably the energy of activation for the pair HP-fuel is lower, meaning that not much thermal energy is spent breaking the bonds. The excess of heat goes to support the detonation process.

It was confirmed that the size of the voids alters the VOD of the mixtures, that is, the larger the size, the lower the VOD.

For this study, it is suggested that the initiation of detonation by hot spots is a combination of a few mechanisms that would depend on the size, construction material and amount of the voids. The mechanisms should coexist in the whole density range of the energetic material and some mechanisms would prevail over others. In addition, the initiation would also depend on the characteristics of the pair oxidiser-fuel and the physical, thermal, and reactive properties of the reacting material at high temperatures.

High speed video footage infers that the temperature reached by the detonation process is different for different densities, and that the observed reaction zone length is much longer than that measured from high explosives.

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