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Sensitizing micron-sized Al/KIO₄ compositions for potential use in
chemical delay detonators

By

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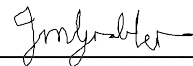
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Declaration

I, Johannes Marthinus Grobler, Student No. 11028727 , do hereby declare that this research is my original work and that to the best of my knowledge and belief, it has not been previously in its entirety or in part been submitted and is not currently being submitted either in whole or in part at any university for a degree or diploma, and that all references are acknowledged.

SIGNED on this 22 day of November 2021



J.M. Grobler

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Abstract

Fast-burning micron-sized compositions were investigated for potential use in chemical delay detonators. This investigation stems from the drive to replace heavy-metal-containing compositions and compounds within these detonators owing to environmental concerns. The Al/KIO₄ composition was modified by adding Al/CuO and Al/PTFE thermites to it to assist with the ignitibility of the composition. The blend of Al/KIO₄/CuO/PTFE had the following mass distribution: 23.56/64.98/7.79/3.68. The addition of copper(II) oxide and PTFE improved the ignitibility of the composition by reducing the ignition temperature of the base composition by approximately 150 °C. With the improved ignitibility came a drastic increase in enclosed combustion performance. The flame front for the sensitised composition approached 1 km·s⁻¹. This is especially remarkable when considering the fact that all components used in the investigation were micron-sized. The increased ignitibility and combustion rate are thought to be due to a change in the ignition mechanism brought about by the addition of the two additional oxidisers. The Al/KIO₄ would have a gas-solid mechanism, while the Al/KIO₄/CuO/PTFE composition is thought to have a combination of gas-solid and condensed phase reactions caused by the pre-ignition reactions between the oxidisers and the native oxide layer on the fuel.

An attempt was made to utilise the composition as a direct replacement for the primary explosive lead azide (Pb(N₃)₂). It was thought that due to its high combustion rate, combustion temperature and the quantity of gas released during its combustion it might be able to initiate multiple reaction zones in a porous pentaerythritol tetranitrate (PETN) bed, thereby accelerating the deflagration to detonation transition. However, this direct replacement was not possible using the detonator shells used commercially since the shells burst before a transition to detonation could occur. The detonator failures were attributed to the comparatively slower transition to detonation that occurs when compared with a primary explosive. The timeframe involved allowed the detonator shell to fail by bursting before a transition could reliably occur. A simple flying plate detonator (FPD) was designed by utilising elements similar to those used for time delays with the addition of a steel flyer. The elements were made from steel as aluminium elements could not contain the pressure. In the trials, the two best-performing designs had muzzle velocities of 434 ± 14 m·s⁻¹ and 475 ± 17 m·s⁻¹. The simple design used compares favourably with PETN initiation data from the literature, indicating that the composition may well find use in lead-azide-free chemical delay detonators.

At this stage however the detonator shells remain the weak link in the design as shell failure occurs before reliable initiation of the PETN base charge used.

Keywords: aluminium thermites, fast burning, sensitisation, burn rate modification.

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Contents

Declaration.....	ii
Abstract.....	iii
Acknowledgements.....	v
List of Figures	x
List of Tables	xiv
List of abbreviations	xv
Nomenclature	xv
1 Introduction.....	1
1.1 Objective.....	2
2 Literature.....	3
2.1 Energetic materials	3
2.1.1 Primary explosives.....	5
2.1.2 Secondary explosives	6
2.1.3 Pyrotechnics	7
2.2 Thermochemistry of energetic materials	7
2.2.1 Heat of reaction	8
2.2.2 Oxygen balance.....	9
2.2.3 Basics of energetic reactions and rates.....	11
2.3 Detonation	15
2.3.1 Shock waves.....	15
2.3.2 Simple theory or ZND model.....	20
2.4 Initiation of detonation.....	22
2.4.1 Shock initiation.....	22
2.4.2 Deflagration to detonation transition (DDT)	25
2.5 Initiators.....	31
2.5.1 Nonelectric initiators.....	31
2.5.2 Electric initiators.....	33
2.5.3 Projectile-based detonator ballistics	35

2.5.4	Deflagration to detonation detonators	47
2.6	PETN.....	47
2.6.1	PETN chemistry and properties	48
2.6.2	Chemical incompatibilities and degradation catalysts.....	50
2.6.3	PETN initiation.....	50
2.7	Fast burning thermites	57
2.7.1	Chemical selection.....	59
2.7.2	Fuels.....	60
2.7.3	Oxidisers.....	62
2.7.4	Additives and binders.....	65
2.7.5	Composition.....	65
2.7.6	Fuel to oxidiser ratio.....	69
2.7.7	Particle size and packing density	69
2.7.8	Processing.....	75
2.8	Fast burning thermites as initiators	77
2.9	Analysis techniques	80
2.9.1	Differential thermal analysis (DTA).....	80
2.9.2	Bomb calorimetry.....	80
2.9.3	Scanning electron microscopy (SEM)	80
2.9.4	X-ray diffraction (XRD) and X-ray fluorescence (XRF)	81
2.9.5	Particle size distribution and surface area.....	82
3	Experimental.....	83
3.1	Materials and characterisation	83
3.1.1	Materials selection	83
3.1.2	Characterisation techniques and methods	83
3.2	Mixing	84
3.2.1	Oxidiser combinations.....	84
3.2.2	Fuel combinations.....	85
3.2.3	Iodine test	85

3.3	Thermal analysis.....	86
3.4	Sensitivity analysis.....	86
3.5	Combustion Performance	87
3.5.1	Burn rates	87
3.5.2	Calorimetry	88
3.5.3	Pressure measurements.....	88
3.5.4	Temperature measurements.....	88
3.6	Detonator tests	89
3.6.1	Preliminary detonator assembly and testing.....	89
3.6.2	Initial tests with the base system.....	89
3.6.3	Improved loading procedure and modifications	90
3.7	FPD detonator design and testing.....	90
3.7.1	Ballistic measurements	91
3.7.2	Detonator testing	95
4	Results.....	96
4.1	Particle size and surface area.....	96
4.2	Microscopy	97
4.3	XRD and XRF results.....	98
4.4	Iodine test	98
4.5	DTA analysis.....	101
4.5.1	Aluminium oxidiser combinations	101
4.5.2	Fuel combinations.....	110
4.6	Sensitivity	114
4.7	Combustion performance and products.	115
4.7.1	Open burns.....	115
4.7.2	Combustion temperature measurements	116
4.7.3	Closed burns.....	116
4.7.4	Calorimetry	117
4.7.5	Burn residue analysis.....	118

4.7.6	Pressure measurements.....	119
4.8	Detonator testing results	122
4.8.1	Preliminary detonator assembly and tests.....	122
4.8.2	Copper shells.....	126
4.8.3	Copper-nickel shells.....	128
4.8.4	Flying plate detonator	129
4.8.5	Ballistic model and improvements.....	142
5	Discussion	147
5.1	Mixing methods.....	147
5.2	Ignitibility, heat of reaction and sensitivity	147
5.3	Combustion performance.....	150
5.4	Detonator trials	152
6	Conclusions and recommendations	154
7	References	156
	Appendix A: XRD and XRF results.....	166

List of Figures

Figure 2-1. Categorisation of energetic materials.	4
Figure 2-2. Shock front traveling from the left through a control volume.	16
Figure 2-3. Examples of (a) U-u, (b) P-V and (c) P-u Hugoniot plots.	19
Figure 2-4. P-V plane representation of detonation.	21
Figure 2-5. Nonelectric pyrotechnic delay detonator modified from (Ziegler, 1987).	32
Figure 2-6. Ballistic breakdown for a projectile.	35
Figure 2-7. Simplified depiction of the forces acting on a projectile while it's in the barrel...	38
Figure 2-8. Depiction of the FPD system, with the barrel directly against the target.	40
Figure 2-9. Projectile velocity change over distance for projectiles of 8 mm, 4mm and 2 mm in diameter with initial velocities of $500 \text{ m}\cdot\text{s}^{-1}$ and $1000 \text{ m}\cdot\text{s}^{-1}$	41
Figure 2-10. (a) Interface pressure, (b) initial shock duration and (c) distance to detonation as a function of initial projectile velocity.	44
Figure 2-11. Pop-plots for PETN at different initial densities, data adapted from Stirpe et al. (1970).	45
Figure 2-12. Circular flyer impact inducing a shockwave in a target explosive and subsequent interaction with rarefaction waves Cooper (1996).	46
Figure 2-13. PETN chemical structure.	48
Figure 2-14. Temperature dependence for the onset of thermal runaway in PETN. Adapted from Henkin and McGill (1952).	51
Figure 2-15. Small scale gap test for PETN indicating the critical pressure relation to PETN density. Adapted from (Bauer, 1975).	52
Figure 2-16. Ellingham diagram for potential fuels adapted from DoITPoMS (2021), oxygen provided at partial pressure of 101.325 kPa.	66
Figure 2-17. Aluminium core volume fraction as a function of particle size.	71
Figure 3-1. Illustration of the experimental setup as well as an example of the silica tube and steel housing used. The camera is indicated by (C), steel collar (SC), bolt (B), steel housing (SH) and silica tube (T).	87
Figure 3-2. Detonator assembly.	89
Figure 3-3. FPD (a) combustion chamber, (b) projectile.	91
Figure 3-4. The open element housing containing an element and fuse head.	92
Figure 3-5. Experimental setup for projectile velocity measurement. The element is indicated by (E), the camera by (C) and the target (T). Three rows of calibration dots are indicated by (D).	92
Figure 3-6. Crater dimensions, depth (z) and radius (a), caused by a rigid penetrator of diameter (D), adapted from (Byrnside and Torvik, 1971).	93

Figure 4-1. SEM imaging for the individual components used in the composition. (a) Aluminium, (b) copper oxide, (c) sulfur (d) PTFE and (e-f) recrystallized potassium periodate.	97
Figure 4-2. Optical microscope images of potassium periodate recrystallized in the presence of aluminium.	98
Figure 4-3. Demonstration of the iodine test without aluminium present. (a) Contains a KIO_4/KI solution, (b) contains a $\text{KIO}_4/\text{dextrin}$ solution, and (c) contains $\text{KIO}_4/\text{dextrin}/\text{KI}$	99
Figure 4-4. Iodine test results. The vial contents at each interval are: (Left) Al/KIO_4 , (middle) $\text{Al}/\text{KIO}_4/\text{dextrin}$, (right) $\text{Al}/\text{KIO}_4/\text{dextrin}/\text{KI}$ and (far-right) $\text{Al}/\text{KIO}_4/\text{KI}$	100
Figure 4-5. DTA response for single components.....	101
Figure 4-6. DTA responses for binary systems.....	103
Figure 4-7. DTA responses for the Al/KIO_4 composition with the addition of the Al/CuO composition at different mass ratios $[\text{Al}/\text{KIO}_4 : \text{Al}/\text{CuO}]$	104
Figure 4-8. DTA responses for the Al/KIO_4 composition with the addition of the Al/PTFE composition at different mass ratios $[\text{Al}/\text{KIO}_4 : \text{Al}/\text{PTFE}]$	105
Figure 4-9. DTA responses for mixtures of the oxidisers.	106
Figure 4-10. DTA responses for systems containing potassium perchlorate.....	107
Figure 4-11. DTA responses for systems containing alumina and potassium iodide.....	107
Figure 4-12. DTA responses for a combination of all three binary compositions. The ratios given are $[\text{Al}/\text{KIO}_4 : \text{Al}/\text{CuO}]$ which is then further blended to contain 5 wt. % PTFE.....	109
Figure 4-13. DTA response for sulfur and its binary compositions.	110
Figure 4-14. DTA response for an Al/KIO_4 composition combined with Al/S at different mass ratios $[\text{Al}/\text{KIO}_4 : \text{Al}/\text{S}]$	111
Figure 4-15. DTA response for an Al/KIO_4 composition combined with an aluminium and S/KIO_4 at different mass ratios $[\text{Al}/\text{KIO}_4 : \text{S}/\text{KIO}_4]$	112
Figure 4-16. DTA response for the $[\text{Al}/\text{KIO}_4:\text{Al}/\text{S}:\text{Al}/\text{PTFE}]$ and the $[\text{Al}/\text{KIO}_4:\text{S}/\text{KIO}_4:\text{Al}/\text{PTFE}]$ blends mixed in a [90:10]:5 the ratio.....	113
Figure 4-17. Diffractogram of combustion products from (A) Al/KIO_4 , (B) $\text{Al}/\text{KIO}_4/\text{CuO}$ and (C) $\text{Al}/\text{KIO}_4/\text{CuO}/\text{PTFE}$ compositions.....	118
Figure 4-18. Pressure response for the compositions in air atmosphere.	120
Figure 4-19. Pressure response for compositions in a 30 bar helium atmosphere.....	120
Figure 4-20. Pressure response for G composition in air and helium.....	121
Figure 4-21. Delay element illustrating density variations in each increment. Increments were added from the right hand side.....	123
Figure 4-22. Detonator assembly, (a) loaded element (b) element in detonator shell and (c) evidence of the misfire.	123

Figure 4-23. The movement of the composition during a firing event as monitored by X-ray imaging. (a) Initial state of the compositions. (b-c) Compression of the compositions due to shock tube output. (d) Composition layers separating. (e-f) composition rebounding back.	124
Figure 4-24. (a) Evidence of gap formation during crimping. (b) Pre-crimping of detonator containing and additional layer of loose G composition. (c) Post crimping of the detonator containing the additional G layer.	125
Figure 4-25. (a) Detonator shell remains from run 5. (b) Remains of a detonator shell that contained erythritol instead of PETN.	125
Figure 4-26. Detonator assembly before (a) and after (b) crimping.....	126
Figure 4-27. Copper shells post burn.	128
Figure 4-28. Copper-nickel shells post burn.	129
Figure 4-29. Witness plate results from detonator trials. (Dents are circled)	129
Figure 4-30. High-speed imaging results for SB7.	132
Figure 4-31. Velocity as a function of barrel length for element types.....	132
Figure 4-32. Examples of failure in the 29 mm tubes (a) and example of an unsupported element burn (b).....	133
Figure 4-33. Three frames from a SB trial showing media other than the projectile being expelled from the barrel.	134
Figure 4-34. (a) Projectile velocity over distance, (b) experimental data fit to calculated velocities.	134
Figure 4-35. Impact demonstration, (a) target at 24 cm from element, (b) target 5 cm from element (c-d) targets in contact with the element.	135
Figure 4-36. SEM imaging of a 3.1 mm thick aluminium target shot by a SB element at 5 cm	135
Figure 4-37. Impact energy and interface pressure for projectiles shot from SB and LB elements.	138
Figure 4-38. Initial shock duration and run distance to detonation for projectiles shot from SB and LB elements.	138
Figure 4-39. X-ray imaging of SB and LB elements in in copper-nickel shells.	140
Figure 4-40. (a) Copper-nickel shells containing long and short barrels post burn. (b) Example of element and subsequent shell failure.	140
Figure 4-41. Witness plates (a) and blocks (b) for long and short barrels.	141
Figure 4-42. Witness blocks and plates for SB and LB element types. Circled area indicates indentation. Arrows indicate potential bearing impact.....	142

Figure 4-43. Down barrel velocity for LB and SB element types. (▲) Average measured muzzle velocity of SB elements. (●) Average muzzle velocity of LB elements. The initial temperature of the chamber was set at 2091 K.	144
Figure 4-44. Effect of barrel length on muzzle velocity.	144
Figure 4-45. Impact of projectile mass on the muzzle velocity of the LB elements.....	145
Figure 4-46. (a) Projectile velocity variation with charge mass. (b) Muzzle velocity variation with charge mass.	145
Figure 1. Diffractogram for aluminium.	166
Figure 2. Diffractogram for potassium periodate.....	166
Figure 3. Diffractogram for copper(II) oxide.	167
Figure 4. Diffractogram for PTFE.....	167
Figure 5. Diffractogram for sulfur.	168
Figure 6. Diffractogram for potassium perchlorate (KClO_4).....	168
Figure 7. Diffractogram for potassium iodide.	169

List of Tables

Table 2-1. Examples of primary explosives (Klapötke, 2012).....	5
Table 2-2. Examples of secondary explosives	6
Table 2-3. Oxygen balance of common explosives	10
Table 2-4. Critical energy requirement for PETN initiation	52
Table 2-5. Examples of fast and or gas generating thermites studied by a variety of authors	58
Table 2-6. Commonly used oxidisers and their melting points	62
Table 2-7. Thermal analysis results of pyrotechnic systems	68
Table 2-8 Effect of fuel and oxidiser size on linear burn rate (Weismiller et al., 2011).....	72
Table 2-9. Effect of density on combustion performance, adapted from Sanders et al. (2007)	74
Table 2-10. Performance comparison between mixing methods for a nano-aluminium sodium periodate based thermite adapted from Wan et al. (2019).....	77
Table 4-1. Particle size distribution and BET surface area for the components used	96
Table 4-2. Sulfur loading in the compositions.	114
Table 4-3. Comparing the ignition sensitivity of base- and sensitised composition to other explosives	115
Table 4-4. Open burn rates for binary systems	115
Table 4-5. Enclosed burn rate results	116
Table 4-6. Average heat of reaction for pyrotechnic compositions used in burn trials	117
Table 4-7. Solid combustion products.	118
Table 4-8. Composition comparison between the as mixed and the calculated compositions from the burn residue assuming all components were accounted for in the analysis	119
Table 4-9. Combustion pressure in air and helium	121
Table 4-10. Preliminary detonator assembly values.....	122
Table 4-11. Loading parameters for copper detonator shells	127
Table 4-12. Loading parameters for copper-nickel shells.....	128
Table 4-13. Slapper elements loading and performance.....	131
Table 4-14. Altered slapper elements loading and performance	131
Table 4-15. Crater dimensions and impact data.....	136
Table 4-16. Calculated velocity comparison.....	136
Table 4-17. FPD element loadings for detonators.....	139
Table 1. Summarised XRF analysis of aluminium and sulfur.	169

List of abbreviations

An	Andreev number
BET	Brunauer–Emmett–Teller
EBW	Exploding bridge wire
EFI	Exploding foil initiator
EOS	Equation of state
ER	Equivalence ratio
DDT	Deflagration to detonation transition
DTA	Differential thermal analysis
MDM	Melt dispersal mechanism
MM	Molar mass
OB	Oxygen balance
PETN	Pentaerythritol tetranitrate
SEM	Scanning electron microscopy
TMD	Theoretical maximum density
XRD	X-ray diffraction
XRF	X-ray fluorescence

Nomenclature

Symbol	Description	Units
A, A_b, A_o	Surface area, projectile base area, specific surface area	$\text{m}^2, \text{m}^2 \cdot \text{kg}^{-1}$
a	Acceleration, Experimental parameter, crater radius	$\text{m} \cdot \text{s}^{-2}, \text{m}$
C	Sound speed in shocked explosive	$\text{km} \cdot \text{s}^{-1}$
$C(M)$	Drag coefficient	
C_i	Initial propellant mass	kg
C_o	Bulk sound speed in material	$\text{km} \cdot \text{s}^{-1}, \text{cm} \cdot \mu\text{s}^{-1}$
C_p, C_v	Heat capacity at constant pressure, heat capacity at constant volume	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
C_s	Free crystal velocity	$\text{cm} \cdot \mu\text{s}^{-1}$
DE	Lattice dissociation energy per atom	$\text{eV} \cdot \text{atom}^{-1}$
d	Plate thickness, interplanar spacing	m
d_h	Hydrolytic pore diameter	m
d_l	Atomic spacing in slip direction	Approx. 10^{-8} cm
E, e	Energy per unit area, Internal energy, specific internal energy	$\text{J} \cdot \text{cm}^{-2}, \text{kJ}, \text{kJ} \cdot \text{g}^{-1}$
E_a	Activation energy	$\text{J} \cdot \text{mol}^{-1}$
E_p	Kinetic energy of propellant mass and unburnt propellant	J
F, F_p, F_f, F_r	Force, propulsion, friction, retardation	N
F/O_a	Fuel to oxidiser mass ratio as mixed	

F/O_s	Fuel to oxidiser mass ratio stoichiometric	
G	Gibbs-energy	$\text{kJ}\cdot\text{kg}^{-1}$
H	Enthalpy	$\text{kJ}\cdot\text{kg}^{-1}$
h	Planck's constant	$\text{g}\cdot\text{cm}^2\cdot\text{s}^{-1}$
KE	Kinetic energy	J
k	Rate constant, material constant, Co-volume constant	
k_o	Pre-exponential constant	s^{-1}
k_ϕ	Dynamic relaxation parameter for explosive bed	$\text{GPa}\cdot\mu\text{s}^{-1}$
l	Chamber length	m
M	Mach number	
m, m_i	Mass, specific mass	kg, $\text{kg}\cdot\text{m}^{-3}$
m_{av}	Average weight of a sing atom in the material	Approx. 10^{-23}g
n	Diffraction order, material constant	
P, p, P_b, P_h	Pressure, Pressure at projectile base, hardening pressure	Pa, GPa
Q	Heat release rate per unit volume, heat released by propellant	$\text{kJ}\cdot\text{s}^{-1}\cdot\text{m}^3$, kJ
R	Ideal gas constant	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Re	Reynolds number	
r	Size variable	cm
r_e, r_λ, r_ϕ	Rate equitation, reaction rate , compaction rate	$\text{s}^{-1}, \mu\text{s}^{-1}, \mu\text{s}^{-1}$
S	Entropy	$\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
S_i	Surface area	m^2
S, s	Medium dependant dimensionless constant, Distance	m
T	Temperature, time of maximum shock	K, s
t	Time	s
U	Shock Velocity	$\text{km}\cdot\text{s}^{-1}$, $\text{mm}\cdot\mu\text{s}^{-1}$
U	Internal energy of propellant gasses	kJ
u	Particle velocity, combustion velocity, velocity in x direction	$\text{km}\cdot\text{s}^{-1}$, $\text{m}\cdot\text{s}^{-1}$, $\text{mm}\cdot\mu\text{s}^{-1}$
u_l	Linear burn rate	$\text{m}\cdot\text{s}^{-1}$
u_m	Mass burn rate	$\text{kg}\cdot\text{s}^{-1}$, $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}$
V	Volume	m^3
V_f, V_l	Phonon fission velocity, Free particle velocity	$\text{cm}\cdot\mu\text{s}^{-1}$
v	Velocity, specific volume	$\text{m}\cdot\text{s}^{-1}$, $\text{cm}^3\cdot\text{g}^{-1}$
v_s	Speed of sound in air	$\text{m}\cdot\text{s}^{-1}$
W, w	External work done on projectile, work	J
x	Projectile displacement	m
Z	Depth	m
Z_i	Fraction of propellant burnt	
Greek		
α	Thermal diffusivity, burning rate index	$\text{m}^2\cdot\text{s}^{-1}$, $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$
α_*	Material constant	$\text{m}\cdot\text{s}^{-1}$
β	Burning rate coefficient, Experimental parameters	
γ	Ratio of specific heats	
δ	Shape factor	
λ	Thermal conductivity of gas	
μ	Viscosity	$\text{Pa}\cdot\text{s}$
ρ	Density	$\text{kg}\cdot\text{m}^{-3}$, $\text{g}\cdot\text{cm}^{-3}$
$\emptyset$	Extent of compaction	

Subscript

AB	Afterburn
<i>a</i>	Air
<i>c</i>	Combustion, Critical
<i>b</i>	Bulk
<i>d</i>	Detonation
<i>e</i>	Explosion
<i>f</i>	Formation, flyer
<i>HE</i>	Explosive
<i>p</i>	Products
<i>r</i>	Reaction, reactants
<i>s</i>	Plate

1 Introduction

Heavy metals and compounds based thereon find widespread use in both military and civilian energetic materials and systems utilising them. The use of these compounds does however come with some environmental implications beyond the initial detonation. Lead and compounds containing it such as lead azide ($\text{Pb}(\text{N}_3)_2$) and lead oxide (Pb_3O_4) are used as, or in, primary explosives, pyrotechnic compositions and ammunition. Upon using these systems lead or its oxides are deposited in the environment leading to a build-up of in the soil and water resources. For this reason there has been a drive to replace or limit the use of these compounds or components.

In certain devices or applications the replacement of a lead based compound or component can be effected by a simple substitution. An example of this is the use of lead free bullets in which the lead core is replaced with a more environmentally friendly substance such as solid copper (Caudell et al., 2012). Staying with ammunition, the primer compositions used to initiate the propellant also contain lead based compounds such as the primary explosive lead azide. Its direct replacement is more difficult since its inclusion in the primer is due to its sensitivity and energetic output. Finding an alternative for it in this application requires a reformulation of the composition.

Initiators are another area of focus for improving the environmentally-friendliness of the energetics industry. This is due to the vast numbers of detonators of various types being used in the mining sector. Depending on the type of detonator, multiple components can contain lead, such as the compositions used in delay columns and the primary explosives. Changing the pyrotechnic time delay compositions to more environmentally benign ones, is relatively simple compared to the replacement of the primary explosive. This is due to the large difference in performance between a detonating primary explosive and a pyrotechnic reaction. Advances in the pyrotechnic field have led to the development of pyrotechnic compositions that burn in excess of $1 \text{ km}\cdot\text{s}^{-1}$. This has led to serious interest in the possibility of using pyrotechnics, especially nano-thermites for primary explosive applications. There are numerous potential benefits to replacing primary explosives in detonators. These include the environmental factors previously mentioned but also immediate safety. Primary explosives are used for their rapid and destructive response to stimuli, but this does come with inherent dangers when handling them. A system that can achieve the same results without the associated environmental impact and safety concerns is therefore preferred.

1.1 Objective

It is well known that nano-thermites have better energetic performance characteristics when compared to micron-sized thermites. For that reason, those compositions have received the primary interest of researchers searching for pyrotechnic alternatives to the primary explosives used in initiation devices. In certain applications this is feasible. However, for certain industries it is problematic due to availability, cost and ease of implementation in manufacturing processes already in operation. One area which could benefit from the use of primary explosive free detonators is the mining sector. Large-scale use of nanocomponent-based devices may however be problematic due to the aforementioned obstacles.

To this end, a micron sized composition needs to be identified that would allow for the replacement of the lead azide used in these detonators. The composition or system in which it is applied should be implementable with minimal changes to the current detonator assembly procedures. This involves the following criteria:

- It should be more stable than lead azide during assembly, storage and handling;
- It should be able to initiate pentaerythritol tetranitrate (PETN) or a similar explosive base charge either through direct action or as part of an initiation device, and
- It should avoid the use of lead-based oxidisers.

2 Literature

Lead and the compounds it forms during its use are well known for having toxic effects (Ilyushin et al., 2012, Jenkins, 2015). Exposure can have negative neurological, cardiovascular and metabolic implications depending on the exposure levels (Jenkins, 2015, Ilyushin et al., 2012). As part of the continuous drive towards green energetic materials and devices, alternatives to lead based compounds are being investigated for use as- or in primers, delay elements, initiation devices and even as projectiles (Steinhauser and Klapötke, 2008, Tichapondwa et al., 2015, Jenkins, 2015).

Finding pyrotechnic alternatives to the lead azide used in chemical delay detonators is a difficult task without redesigning the detonator construction. Khasainov et al. (2017) mention that direct replacement of primary explosives with thermites is unlikely to succeed. The problem is that the reaction rate of thermites, even nano-thermites, are significantly slower than that of a detonating primary explosive which is in excess of $3.5 \text{ km} \cdot \text{s}^{-1}$ (Klapötke, 2012). The resulting compression waves generated by a detonating primary explosive is 2-3 orders of magnitude larger than that of a fast burning nano-thermite (Khasainov et al., 2017). Alternative initiation methods therefore need to be investigated. There are examples of initiators that do not contain primary explosives. The flying plate detonator (FPD) is an example of such a device, which uses the shock caused by the impact of a projectile to initiate a secondary explosive. Recent designs, e.g. the one proposed by Glavier et al. (2017), employed a nano-energetic material to propel the flyer. Realising the full potential of these systems, requires a deeper understanding of energetic materials and how the different classes interact with each other and with external stimuli.

2.1 Energetic materials

The discovery of black powder is the most likely origin of the relationship man has with energetic materials (Oxley, 2003). It took centuries however, before science and industry moved beyond the simple mixture of potassium nitrate (KNO_3), charcoal and sulfur (S). Black powder, like the other energetic materials that followed, undergo a highly exothermic oxidation reaction. These are the reactions which are harnessed for a variety of civilian and military applications.

Combustion processes of energetic materials can be defined as oxidation reactions which are exothermic and self-sustaining even in the absence of atmospheric oxygen (Akhavan, 2004, Johansson and Persson, 1970). Energetic materials are classified according to their

application and/or how they react. Figure 2-1 lists the major categories of energetic materials according to their properties (Klapötke, 2012, Venugopalan, 2015).

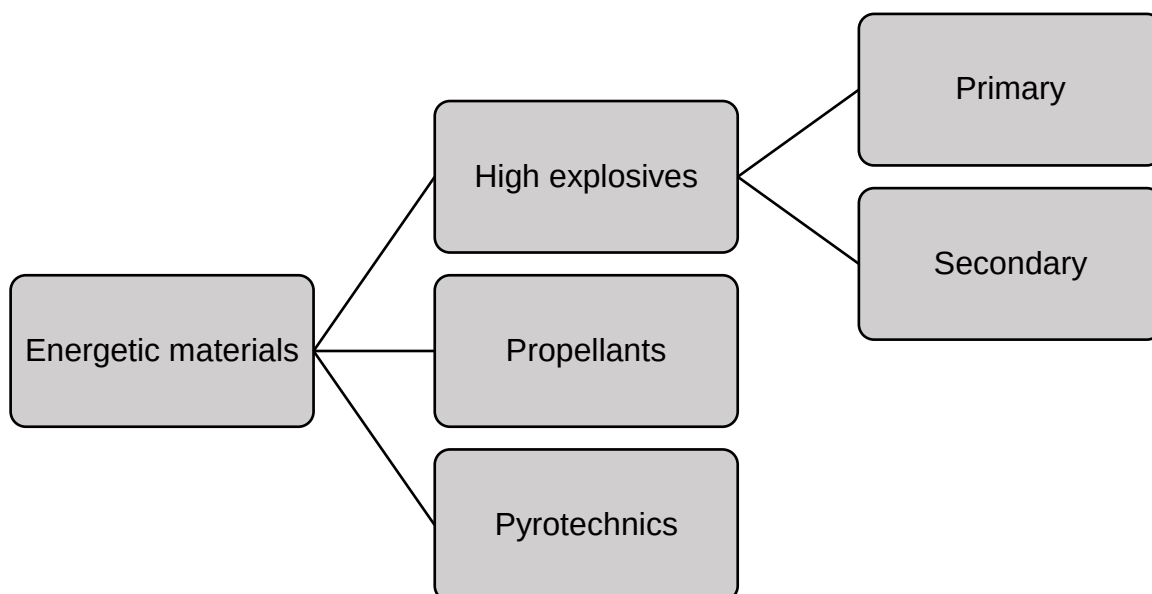


Figure 2-1. Categorisation of energetic materials.

The way in which these classes of energetic materials react will be explained in further detail later on. For now, it is sufficient to know that the rate of reaction decreases from high explosives to pyrotechnics. The classification shown are not rigid as there are a number of compounds or compositions that find use outside of their primary group.

An explosion is a process during which energy, that was confined previously, is released rapidly (Fordham, 1980). Explosives are defined as substances or mixtures of substances that when initiated in an appropriate manner can produce quantities of gas at sufficiently high pressures and rates to subject the surroundings to strong dynamic stress (Fordham, 1980, Handley et al., 2018). When the reaction is driven by a shock front, and proceeds at the rate of the passing shock, it is classified as a detonation.

Not all energetic materials react in an explosive manner, propellants undergo deflagrations while the rate of pyrotechnics reactions range from slow combustion to deflagration. Deflagrating materials react faster than “ordinary” combustible materials, during the reaction the flame front will proceed at a significant speed with an audible noise yet it will remain at a subsonic velocity (Akhavan, 2004, Johansson and Persson, 1970, Klapötke, 2012). Deflagration reactions are unstable in nature and they can slow down or even accelerate to detonation (Comet et al., 2015).

2.1.1 Primary explosives

Compared to secondary explosives, primary explosives are very sensitive towards external stimuli (Klapötke, 2012, Khasainov et al., 2017, Fordham, 1980). They undergo a rapid transition from deflagration to detonation (Klapötke, 2012, Khasainov et al., 2017, Fousson et al., 2016). This property makes them useful for use in initiating devices where they are used to initiate or transfer a detonation event to a more stable secondary explosive. The violent nature of the reaction produces a shockwave which transfers the detonation event to the secondary explosive (Klapötke, 2012). Table 2-1 shows examples of primary explosives.

Table 2-1. Examples of primary explosives (Klapötke, 2012)

Name	Formula
Mercury fulminate	$\text{Hg}(\text{CNO})_2$
Lead azide	$\text{Pb}(\text{N}_3)_2$
Lead styphnate	$(\text{NO}_2)_3\text{C}_6\text{HO}_2\text{Pb}$
Cadmium azide	$\text{Cd}(\text{N}_3)_2$
Silver acetylide nitrate	$\text{Ag}_2\text{C}_2 \cdot 6\text{AgNO}_3$

A common feature of the components listed in Table 2-1 is that they contain heavy metals. As mentioned, they are associated with environmental concerns. For this reason, and the inherent dangers accompanying their use and handling, much research has been conducted into potential replacements (Fousson et al., 2016, Glavier et al., 2015, Du et al., 2013, Klapötke, 2012, Comet et al., 2015). In a detonator the primary explosive has to initiate a detonation event in the secondary explosive base charge. This requires a significant stimulus. The ability to accept a relatively low energy signal and “convert” it into a high energy output rapidly is what makes these compounds so useful in this application. It is also the reason why direct replacement is proving to be difficult. Khasainov et al. (2017) and Huynh et al. (2006) listed the criteria necessary for a compound or a mixture to act as a replacement for primary explosives:

- High initiating capacity;
- Safe during handling and application;
- Good flowability and compressibility;
- Chemically stable in the intended environment of application, and
- Any additional constraints determined by the application.

Finding a suitable replacement therefore requires balancing of the abovementioned criteria with economic viability. Due to the widespread use of these compounds in a variety of

components of energetic systems it cannot be expected that a single composition or compound can be used as a replacement for all applications. A replacement would more likely have to be tailored to each intended application.

2.1.2 Secondary explosives

Secondary explosives are metastable compounds that react to form gaseous products at high temperatures and pressures (Dobratz and Crawford, 1985, Oxley, 2003). The expansion of these high temperature product gasses is what makes them useful. When the compounds burn in a controllable manner they are or can be used as propellants for rocket motors. Alternatively, the destructive power of detonations is utilised in mining, demolition and military applications.

Like primary explosives, secondary explosives can undergo a detonation event. The difference is that initiation of such an event generally requires a much greater stimulus than that required to initiate the former. For instance, a small mass of a secondary explosive can detonate when subject to a strong shock. However, a thermal stimulus will usually be insufficient to effect a deflagration to detonation transition (DDT) (Dobratz and Crawford, 1985, Klapötke, 2012). Typically, secondary explosives offer significantly higher performance than primary explosives with detonation velocities exceeding $6 \text{ km} \cdot \text{s}^{-1}$ (Klapötke, 2012). Table 2-2 contains examples of secondary explosives.

Table 2-2. Examples of secondary explosives

Name	
PETN	Pentaerythritol tetranitrate
RDX (Research department explosive, hexogen)	1,3,5-trinitro-1,3,5-triazacyclohexane
Tetryl	2,4,6-trinitrophenylmethylnitramine
TNT	2, 4, 6-Trinitrotoluene

TNT is widely used to produce castable explosives. It serves as the base material to which additives such as oxidisers or other high explosive compounds can be added. (Cooper, 1996). Both PETN and RDX find use in blasting cap output charges and in explosive compositions. Examples include pentolite, a castable explosive consisting of TNT and PETN, C-4 which is RDX based plastic explosive, and other rubberised or extrudable compositions (Cooper, 1996).

2.1.3 Pyrotechnics

Pyrotechnic compositions are high energy mixtures that consist of one or more solid fuels mixed with one or more solid oxidisers. This differs from the high explosives mentioned earlier which contain fuel and oxidising components within the same molecule. A well-known example is the reaction between aluminium (Al) and iron oxide (Fe_2O_3). Energetic materials of this kind react significantly slower than their detonating counterparts. This is due to the fuel and oxidiser being physically separate as two different compounds. The relative distance that the reactants have to travel is vast when compared to high explosives where the reactants are in the same molecule. Thermites or pyrotechnic mixtures are used in cutting devices, time delay columns, and in incendiary devices to name just a few of their applications. These applications differ greatly and so do the compositions.

Thermites, especially nano-thermites, have gained significant interest in the energetic materials community due to the high energy density of these compositions (Khasainov et al., 2017, Sullivan et al., 2014, Baijot et al., 2015, Martirosyan et al., 2012). It has been suggested that these materials may offer significant improvements over traditional high explosives in munitions as well as be potential replacements for primary explosives to produce lead-free primers and detonators (Sanders et al., 2007, Glavier et al., 2015, Wang et al., 2011, Baijot et al., 2015). However, up to this point no direct initiation of a secondary explosive with a thermite has been reported (Khasainov et al., 2017). However, hybrid systems have been developed which are in fact lead-free (Khasainov et al., 2017, Glavier et al., 2017, Comet et al., 2015).

2.2 Thermochemistry of energetic materials

Detonation and combustion are both examples of exothermic oxidation reactions. During these reactions heat is evolved due to the reaction products occupying a lower internal energy state than the reactants (Cooper, 1996). When designing a pyrotechnic mixture to perform a certain task it is important to consider the reaction rate and spontaneity. (Conkling and Mocella, 2019). The spontaneity of the reaction relies on the change in Gibbs-energy (ΔG). This change can be calculated with Equation 2-1.

$$\Delta G = G_{(products)} - G_{(reactants)} = \Delta H_r - T\Delta S \quad 2-1$$

In order for the reaction to be spontaneous at constant temperature and pressure the Gibbs-energy needs to be negative and have a sufficiently large value (Conkling and Mocella, 2019). The other variables in Equation 2-1 are the enthalpy or heat of reaction (ΔH_r), temperature (T) and the entropy change (ΔS). In order for a reaction to be spontaneous it is necessary to have

a negative heat of reaction and a large positive value for the change in entropy, as is the case for an explosive reaction (Venugopalan, 2015). Reacting systems that release heat and gaseous products are therefore favoured thermodynamically (Conkling and Mocella, 2019).

2.2.1 Heat of reaction

The heat of reaction is determined from the difference in the heat of formation (ΔH_f) of the products and reactants as shown in Equation 2-2.

$$\Delta H_r = \sum \Delta H_{f(products)} - \sum \Delta H_{f(reactants)} \quad 2-2$$

Heat of formation data is usually available for constituents at standard conditions. This means a pressure of 1 atmosphere and a temperature of 298.15 K. The heat of reaction calculated will therefore have to be adjusted to the appropriate temperature using heat capacity data (Smith et al., 2005). There are several special cases of heat of reaction to consider (Cooper, 1996):

- Heat of combustion (ΔH_c);
- Heat of explosion (ΔH_e);
- Heat of detonation (ΔH_d); and
- Heat of after burn (ΔH_{AB}).

The heat of combustion correspond to the enthalpy change observed when a substance reacts with elemental oxygen resulting in its most oxidised form. The heats of explosion or detonation are applicable to the chemical reactions that occur when a propellant burns or a detonation occurs (Cooper, 1996). Detonations are complex occurrences and the exact nature can vary greatly for the same explosive. It depends on a variety of factors such as initial density, temperature, confinement and morphology (Cooper, 1996). Ideally, the heat of detonation and explosion are determined experimentally. If that is not possible, a reasonable estimate can be made using the ideal product hierarchy rules which state that (Cooper, 1996, Venugopalan, 2015):

1. All of the available nitrogen reacts to form N_2 ;
2. All of the available hydrogen reacts with available oxygen to form water;
3. The oxygen remaining after step (2) reacts with the carbon to form carbon monoxide (CO);
4. If there is still free oxygen available, it reacts with the carbon monoxide to form some carbon dioxide (CO_2);
5. Any excess oxygen remaining at this point stays put as O_2 ; and

6. If all oxygen has been consumed previously remaining carbon forms C(s).

This is just an example of a commonly used hierarchy. Others are available and they may offer better or worse results depending the explosive in question (Cooper, 1996). In the case where an explosive has a negative oxygen (*OB*) balance (see definition given below) the combustion products are not fully oxidised. In that case the heat of after burn should be taken into account. Under these conditions, the formation of detonation products such as carbon monoxide or free carbon will occur. These products are themselves considered fuels and will undergo combustion reactions in the presence of atmospheric oxygen should the ambient temperatures be sufficiently high to ignite them (Cooper, 1996, Lebel et al., 2014). This causes an after burn or secondary fireball that releases heat which is equal to the difference between the heat of combustion and detonation of the original explosive as shown by Equation 2-3 (Cooper, 1996).

$$\Delta H_{AB} = H_c - H_d \quad 2-3$$

The heat released by such a fireball can exceed that of the detonation itself should the detonation products be able to completely react with the surrounding oxygen (Lebel et al., 2014, Cooper, 1996).

2.2.2 Oxygen balance

The oxygen balance indicates the deficit or excess oxygen in a compound or composition required for complete oxidation (Venugopalan, 2015). For an explosive with elemental composition given by $C_xH_yN_wO_z$, the oxygen balance is calculated using Equation 2-4 (Venugopalan, 2015, Cooper, 1996).

$$OB = \frac{MM_{O_2} \cdot 100}{MM_{explosive}} \left(z - 2x - \frac{y}{2} \right) \quad 2-4$$

Equation 2-4 requires knowledge of the molar mass ($MM_{explosive}$) of the explosive as well as the ratios in which the particular elements are present in it. Table 2-3 lists the oxygen balances of some common explosives.

Table 2-3. Oxygen balance of common explosives

Explosive	OB (%)
Ammonium nitrate	+20
PETN	-10.13
RDX	-21.6
Nitroglycerine	+3.5
TNT	-74

The explosives listed in Table 2-3 is just a small sample of what is available. However the general trend, that most explosives have a negative oxygen balance, is exemplified in the Table (Venugopalan, 2015). A negative oxygen balance indicates that the explosive material does not contain enough oxygen within itself to oxidise all of the components to the fullest extent. This can lead to potentially hazardous situations due to the release of toxic products of reaction such as carbon monoxide (Akhavan, 2004).

A positive oxygen balance is unnecessary as excess oxygen serves no purpose. The ideal case would be to have an oxygen balance of zero (Venugopalan, 2015). The oxygen balance affects the overall heat of explosion (Venugopalan, 2015). This should be evident from Equation 2-3 as the heat of combustion is larger than that of the heat of explosion in cases where the oxygen balance is negative. An oxygen balance of zero would imply that all of the detonation products would be in their fully oxidised state thereby maximising the energy released by the reaction.

In the case of pyrotechnic compositions, a similar variable to the oxygen balance is used to describe the ratio of fuel to oxidiser. This is known as the equivalence ratio (*ER*), the calculation of which is shown in Equation 2-5 (Dean et al., 2010, Prentice et al., 2006, Apperson et al., 2007, Yen and Wang, 2012).

$$ER = \frac{F/O_a}{F/O_s} \quad 2-5$$

The fuel to oxidiser mass ratio is depicted by F/O_s with the subscripts for depicting actual and stoichiometric values shown as *a* and *s* respectively. A stoichiometric mixture will have an equivalence ratio of one while fuel rich systems will have an equivalence ratio exceeding unity. As with the oxygen balance, the equivalence ratio affects the combustion properties and performance of the pyrotechnic composition.

Substantial deviations from the stoichiometric mixture composition can drastically alter a system's performance. Should the equivalence ratio be significantly smaller than unity, the composition will most likely not burn in a self-sustained manner. Slightly fuel rich mixtures usually show improved ignition behaviour as well as higher linear propagation rates when burnt in the presence of atmospheric oxygen (Pantoya and Granier, 2005, Bockmon et al., 2005, Focke et al., 2018).

2.2.3 Basics of energetic reactions and rates

2.2.3.1 Decomposition reactions for explosives

Explosive materials slowly decompose even at temperatures approaching absolute zero (Cooper, 1996, Akhavan, 2004, VA, 1974). If decomposition is only temperature dependant it is described by a zero order rate equation (r_e) given in Equation 2-6 (Cooper, 1996).

$$r_e = k(T) = k_o e^{\frac{-E_a}{RT}} \quad 2-6$$

The symbols k , k_o , R , T and E_a indicate the rate constant, pre-exponential constant, ideal gas constant, temperature and activation energy respectively. It should be noted that for most explosives zero order decomposition kinetics are only valid for low temperatures such as those that an explosive might experience during its storage (Cooper, 1996). At elevated temperatures such as those experienced during combustion reactions other effects can accelerate decomposition.

The rate at which heat (Q) is evolved by the decomposition reaction can be determined by Equation 2-7 (Cooper, 1996).

$$Q = \rho \Delta H_r k \quad 2-7$$

Transfer of the heat produced to the surroundings depends on the heat capacity (C_p), density (ρ), thermal conductivity (λ) and the temperature of the material (Cooper, 1996). The temperature of the material will increase should the rate at which heat is evolved be faster than that at which it is dissipated into the environment. Equation 2-8, known as the Frank-Kamenetskii Equation, depicts the relationship between heat production to the rate of temperature change (Dobratz and Crawford, 1985).

$$-\lambda \nabla^2 T + \rho C_p \left(\frac{dT}{dt} \right) = Q \quad 2-8$$

This relationship is used to calculate the time to detonation and critical temperature (T_c) for certain geometries. The critical temperature is the minimum temperature at which a high explosive will self-heat to explosion (Dobratz and Crawford, 1985). Solving Equation 2-8 for a given geometry at infinite time results in Equation 2-9 (Dobratz and Crawford, 1985, Cooper, 1996).

$$\frac{E_a}{T_c} = R \ln\left(\frac{r^2 \rho Q E_a}{T_c^2 \lambda \delta R}\right) \quad 2-9$$

The geometry of the explosive is taken into account by the shape factor (δ). It has a value of 0.88 for an infinite slab, 2 for an infinite length cylinder and 3.32 for a sphere. The dimensions of the explosive mass in question is accounted for with variable (r). It is equal to the radius of a sphere, cylinder and in the case of an explosive slab it is half its thickness. Equation 2-9 is a useful tool for determining safe storage conditions such as the maximum charge size that can be stored at a specific temperature (Cooper, 1996).

2.2.3.2 Combustion reactions

Combustion of reactive gasses and solid energetic materials are similar (Kubota, 2002). Combustible solids need to undergo some physiochemical changes before reacting. An example of this can be a strand ammonium perchlorate. The combustion reaction is an exothermic reaction. A portion of the heat released will be fed back to the underlying solid material. Leading to phase changes and decomposition of the exposed surface material providing the reactants necessary for the reactions (Kubota, 2002). This means that the combustion front travels layer by layer from the spent fuel to the unreacted fuel. Should the heat released by the reactions behind the front be insufficient to sustain the movement of the of the flame front the reaction will be quenched if no external heat source is available (Kubota, 2002, Andersen, 1965).

When a mixture of fuel and oxidiser burns it can form one of two flame types, premixed and diffusion flames (Kubota, 2002). Premixed flames consist of fuel and oxidiser components that are premixed before the reaction zone allowing the reaction to proceed homogeneously within the combustion zone (Kubota, 2002). An example of this is a gas mixture of methane (CH_4) and oxygen (O_2). On the other hand diffusive flames occur when there is physical separation of the components. The components would therefore need to diffuse into each other in the combustion zone (Kubota, 2002). Diffusion flames progress at a slower rate due this transport related delay. Energetic solids can burn utilising either mode depending on the composition.

For example double-base propellants burn with a premixed flame, whereas a composite propellants can burn with a diffusion flame (Kubota, 2002)

Conductive burn. In conductive combustion reactions the dominant form of heat transfer is conduction. The major factor controlling the burn rate is thermal diffusivity (α), see Equation 2-10 (Asay, 2010).

$$\alpha = \frac{\lambda}{\rho C_p} \quad 2-10$$

Thermal diffusivity is related to thermal conductivity, density and specific heat capacity of the material. External factors such as pressure and temperature also affect the rate at which combustion front progresses (Asay, 2010).

The rate at which an explosive mass burns will increase as the bulk temperature of that explosive increases (Asay, 2010). This is because less conductive heating is required to heat layers adjacent to the reaction zone to the appropriate temperature. As long as the bulk of the explosive remains at a temperature lower than the critical temperature, the burn rate will increase with a rise in temperature. In the case where the temperature exceeds the critical temperature a cook-off event can occur. In this instance ignition of the bulk will occur in a rapid runaway reaction which can result in explosive effects.

Increasing the pressure will lead to higher gas density, thereby allowing for a greater rate of collision between the reactant molecules in the gas phase (Asay, 2010). This increased collision rate increases the rate of reaction. Furthermore, the elevated reaction rate will decrease the reaction zone width, effectively shortening the distance for heat transfer between the reaction zone and the surface of the combustible material (Asay, 2010). Surface regression will therefore accelerate as pressure increases. The rate at which this surface reaction proceeds can be calculated from Equation 2-11 (Akhavan, 2004, Venugopalan, 2015, Asay, 2010).

$$u_l = \beta P^\alpha \quad 2-11$$

The linear burn rate (u_l) increases with the surface pressure of the explosive material. The burning rate coefficient (β) is a function of temperature (Klapötke, 2012). While the burning rate index (α) describes the pressure dependence (Klapötke, 2012). The burning rate index is determined experimentally from burn tests conducted on the explosive material at various

pressures and has been found to range between size from 0.3 to greater than 1 (Akhavan, 2004). For explosives and propellants the burning rate index is usually equal to 1 while thermites have significantly smaller values (Khasainov et al., 2017). Detonations have burning rate index values greater than unity.

Equation 2-11 works for relatively low pressures while the form shown in Equation 2-12 is better suited when operating at higher pressures (Asay, 2010).

$$u_l = a + \beta P^\alpha \quad 2-12$$

In order to obtain the mass velocity (u_m) density and area (A) needs to be taken into account as illustrated in Equation 2-13 (Akhavan, 2004, Klapötke, 2012). Alternatively Equation 2-14 can be used to calculate mass velocity (Luk'yanchikov et al., 2010).

$$u_m = u_l A \rho \quad 2-13$$

$$u_m = \alpha_* P \quad 2-14$$

The pressure in Equation 2-14 is in Pascal and material constant (α_*) has units of $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. This results in a mass burn rate with units of $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}$.

Convective burn. If a porous material is burned in a confined environment a transition from conductive to convective combustion can occur. The transition from a “normal” or conductive burn, to a convective burn drastically increases the burn rate due to an increase in the heat transfer rate (Khasainov et al., 2017, Bobolev et al., 1966).

Convective heat transfer accelerates the burn front by allowing pre-heating the bed ahead of the reaction zone due to gas jets penetrating the porous unreacted medium (Bobolev et al., 1966, Asay, 2010). The transition from conduction to convection-controlled combustion is important for the initiation of detonation reactions. The Andreev criterion (An) can be used to determine whether the transition occurs. It can be calculated by Equation 2-15, and Equation 2-16 (Bobolev et al., 1966, Prentice et al., 2006, Khasainov et al., 2017).

$$An = \frac{\rho_b u_l d_h C_p}{\lambda} = \text{const} \quad 2-15$$

$$d_h = 4\varphi[A_o(1 - \varphi)] \quad 2-16$$

Andreev criterion is a dimensionless constant related to the material properties of the explosive, propellant or thermite and the reaction products. The criteria were originally developed for coarse grains of explosives which produce only gaseous combustion products (Khasainov et al., 2017, Bobolev et al., 1966). However, it has been applied to thermites in order to assess the effect of bulk density (ρ_b) on the convective dominance of a system (Prentice et al., 2006). It incorporates the combustion gasses through the thermal conductivity of the gas term (λ). The hydrolytic pore diameter (d_h) requires knowledge of the porosity (ϕ) as well as the specific surface area (A_o). Below a certain Andreev criterion value, the critical value, a material will remain in stable conduction controlled burning (Khasainov et al., 2017, Bobolev et al., 1966).

2.3 Detonation

In detonating materials the reaction front moves through the unreacted material at a speed greater than that of sound in the specific material (Klapötke, 2012). The decomposition of unreacted material is initiated by a shock wave and is therefore not restricted by heat transfer as is the case with deflagration or combustion (Akhavan, 2004, Johansson and Persson, 1970, Klapötke, 2012). The velocity of this detonation wave depends on the density of the material it is traveling through (Taylor and Weale, 1938).

A rapid exothermic chemical reaction occurs immediately behind the shock front (Cooper, 1996). The thickness of this reaction zone is approximately 0.2 mm (Johansson and Persson, 1970, Klapötke, 2012). The conditions towards the end of this zone are extreme with pressures exceeding 3300 MPa, temperatures greater than 3000 K and significant density increases (Klapötke, 2012, Johansson and Persson, 1970, Taylor and Weale, 1938).

2.3.1 Shock waves

Understanding shock waves are of critical importance when analysing detonations. As they are both the manner in which they are initiated as well as transmitted. A shock wave can be considered to be a discontinuity. There is no gradual transition between the state of the matter before and after a shock wave (Cooper, 1996, Taylor and Weale, 1938). Figure 2-2 illustrates a right moving shock in an unreactive medium.

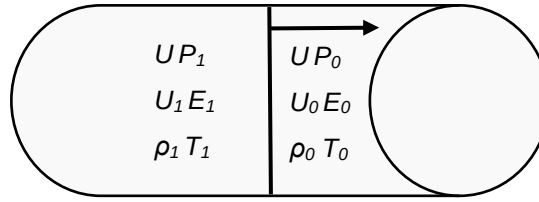


Figure 2-2. Shock front traveling from the left through a control volume.

Subscripts of 1 and 0 in Figure 2-2 indicate shocked and undisturbed material respectively. Momentum mass and energy need to be conserved across the front. The Equations describing the relation between the initial and final states for the variables depicted in Figure 2-2 are known as the Rankine Hugoniot jump equations (Cooper, 1996).

The conservation of mass is depicted by Equations 2-17 to 2-21 (Cooper, 1996, Johansson and Persson, 1970).

$$m = \rho V \quad 2-17$$

$$V = LA \quad 2-18$$

$$L = t(U - u) \quad 2-19$$

$$m = \rho_0 At(U - u_0) = \rho_1 At(U - u_1) \quad 2-20$$

$$\frac{\rho_1}{\rho_0} = \frac{(U - u_0)}{(U - u_1)} = \frac{V_0}{V_1} \quad 2-21$$

Mass (m) is equal to the product of density and volume (V) as shown by Equation 2-17. Volume is a function of length (L) and area. The cross-sectional area of the control volume remains constant, however the distance a particle travels relative to the shock front varies. This is shown by the change in length with time. Shock velocity is depicted by U and the particle velocity is depicted by u . Substitution of Equations 2-18 and 2-19 into Equation 2-17 yields Equation 2-20. Since mass remains constant within the control volume Equation 2-20 can be reorganised as shown by Equation 2-21.

The momentum balance implies that the rate of change in momentum for the control-volume to go from the unshocked to shocked state is equal to the force (F) applied to it. The derivation of the momentum Equation is illustrated in Equations 2-22 through 2-26 (Cooper, 1996)

$$F = (P_1 - P_0)A \quad 2-22$$

$$\text{Rate of change in momentum} = \frac{(mu_1 - mu_0)}{t} \quad 2-23$$

Substituting mass from Equation 2-17 into Equation 2-23 results in Equation 2-24.

$$\text{Rate of change in momentum} = (\rho_1 A (U - u_1)u_1 - \rho_0 A (U - u_o)u_o) \quad 2-24$$

Since the rate of change in momentum is equal to the force applied to the control volume, Equations 2-22 and 2-24 can be equated to deliver Equation 2-25 with some rearrangement.

$$(P_1 - P_0) = \rho_1 (U - u_1)u_1 - \rho_0 (U - u_o)u_o \quad 2-25$$

Combining Equation 2-20 with Equation 2-25 yields Equation 2-26.

$$P_1 - P_0 = \rho_0 (u_1 - u_o)(U - u_o) \quad 2-26$$

The work (w) done on the control volume is can be calculated with Equation 2-27. (Cooper, 1996).

$$\frac{w}{t} = P_1 A u_1 - P_o A u_o \quad 2-27$$

The rate at which the energy increases within the control volume is equal to the sum of the internal (E) and kinetic energy (KE). Internal energy is equal to the product of mass and specific internal energy (e). The rate of change for each of these are shown by Equations 2-28 and 2-29 respectively.

$$\frac{E}{t} = \frac{(\rho_1 A L_1 e_1 - \rho_o A L_o e_o)}{t} \quad 2-28$$

$$\frac{KE}{t} = \frac{0.5(\rho_1 A L_1 u_1^2 - \rho_o A L_o u_o^2)}{t} \quad 2-29$$

The sum of these two equations is set to equal Equation 2-27. Substituting Equations 2-19 and 2-20 into the resultant equation yields Equation 2-30.

$$e_1 - e_o = \frac{P_1 u_1 - P_o u_o}{\rho_0 (U - u_o)} - \frac{1}{2}(u_1^2 - u_o^2) \quad 2-30$$

Equations 2-20, 2-26 and 2-30 are the conservation equations in order to solve the set of equations more relationships are needed. The first of these relationships relates shock velocity to the particle velocity as shown by Equation 2-31 (Cooper, 1996, Johansson and Persson, 1970).

$$U = C_o + su \quad 2-31$$

Equation 2-31 indicates a linear relationship between the shock and particle velocities. The bulk sound velocity through the medium is depicted by C_o while the slope (s) is a dimensionless constant dependant on the medium. This equation describes the U-u plane. The two other Hugoniot planes that are of importance for shock calculations are the P-V and P-u planes as shown by Equations 2-32 and 2-33 respectively (Cooper, 1996).

$$P = C_o^2 (V_o - V) [V_o - s(V_o - V)]^{-2} \quad 2-32$$

$$P_1 = \rho_o u_1 (C_o + su_1) \quad 2-33$$

Both of the preceding equations are derived from the mass and momentum relations derived earlier with initial pressure and particle velocities equal to zero. Using these coordinates the shock wave is viewed from the perspective of the material. Representations of Equations 2-31 to 2-33 are shown in Figure 2-3.

The straight line in Figure 2-3 (b) is an example of a Rayleigh line. The equation describing this line with an initial particle velocity of zero is shown by Equation 2-34 (Cooper, 1996).

$$P_1 - P_o = \frac{U^2}{V_o} - \frac{U^2}{V_o^2} V_1 \quad 2-34$$

The Rayleigh line runs between the initial and final state of the material. It represents the locus for the states of the material as it moves through the region of steady flow while the Hugoniot is the locus for all the possible states behind the shock front (Cooper, 1996, Johansson and Persson, 1970). The slope of Equation 2-34 is dependent on the unshocked density of the material.

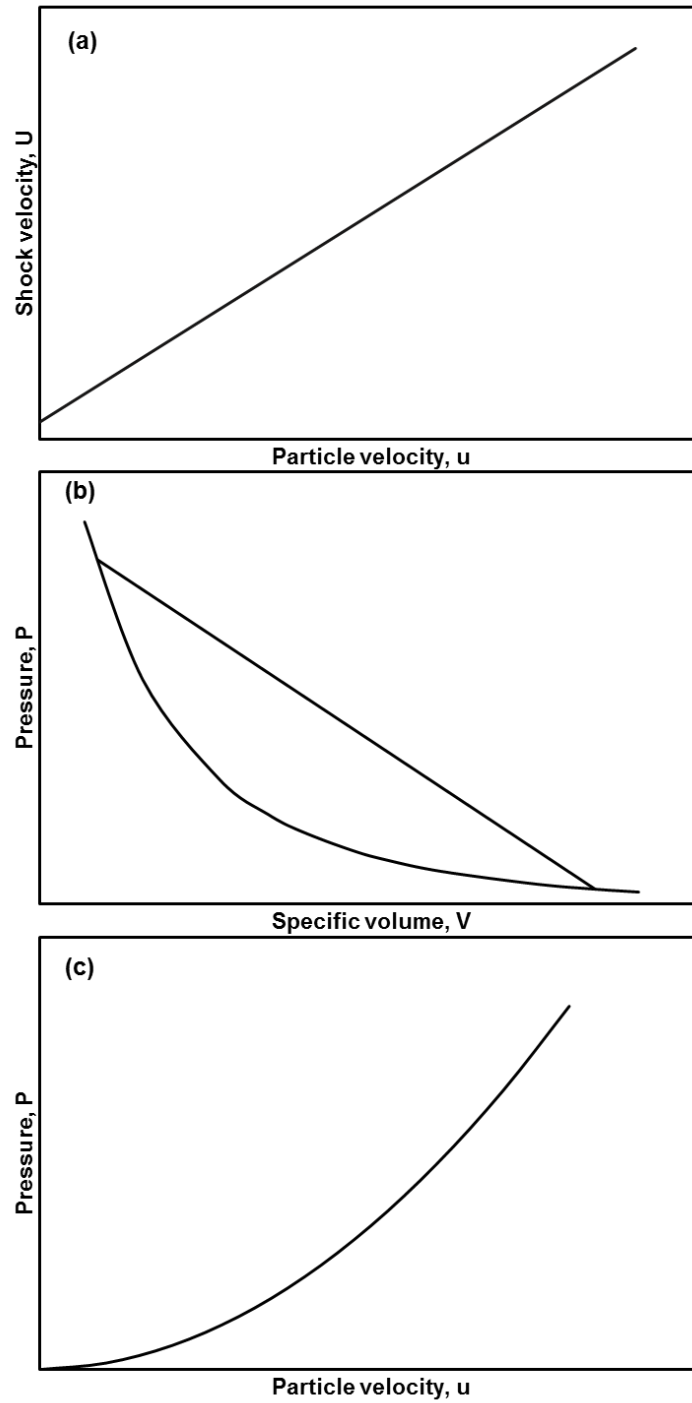


Figure 2-3. Examples of (a) U - u , (b) P - V and (c) P - u Hugoniot plots.

2.3.2 Simple theory or ZND model

The ZND model describes steady ideal detonation. It was independently developed by Zeldovich, Von Neumann and Deering in 1940 (Cooper, 1996). The theory utilises the following assumptions (Cooper, 1996):

1. One dimensional flow.
2. The detonation front is a jump discontinuity.
3. Product gasses leaving the detonation front are in chemical and thermodynamic equilibrium and the reaction is complete.
4. The chemical reaction zone length is taken to be zero.
5. Detonation is a steady-state process.
6. Gaseous reaction products leaving the reaction zone are affected by boundary conditions and surrounding system and can therefore be time dependant.

A detonation event can therefore be described as a moving shockwave that compresses and heats the material as it moves through the explosive in the process initiating an exothermic chemical reaction. Since the assumption is made that the reaction reaches completion in a reaction zone length of zero it has to be instantaneous. The shock front, chemical reaction and leading edge of rarefactions are all in equilibrium (Cooper, 1996). Indicating that they are all moving at the same speed, known as detonation velocity (D). For this reason the front of the shock retains its shape and the detonation velocity remains constant with time (Cooper, 1996, Klapötke, 2012).

When the shock front stops accelerating through the explosive it is called the stationary state (Klapötke, 2012). At this point the free energy released through the exothermic chemical reaction is equal to the heat released to the environment plus the energy needed to compress and move the explosive crystal (Klapötke, 2012). This process can be described on a P-V diagram as is illustrated in Figure 2-4.

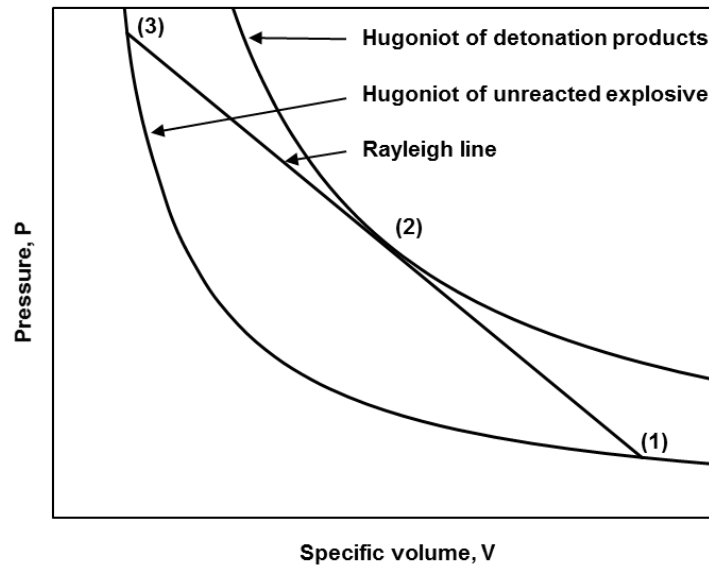


Figure 2-4. P-V plane representation of detonation.

The process shown in Figure 2-4 is valid for “ideal” or homogeneous explosives (Cooper, 1996, Klapötke, 2012). Starting at position (1), the unreacted explosive material is compressed to point (3). This compression to higher pressure and density causes the temperature rise which initiates the reaction. The reaction ends at point (2) which corresponds to the point where the Rayleigh line is tangent to the Hugoniot of the detonation products (Klapötke, 2012). Point (2) is called the Chapman-Jouguet (CJ) point (Cooper, 1996). This point provides information regarding the state detonation products as the pressure and specific volume of the combustion products is known. In the case where the Rayleigh line lies below the product Hugoniot curve, the jump would not include those products. Should the Rayleigh line intersect the product Hugoniot then there is potential for two product states. However, this is impossible since the rarefaction waves and the shock velocity will not be in equilibrium thereby breaching the constraints discussed earlier (Cooper, 1996). At first glance it may seem that the process follows a curve but it should be remembered that the process entails a jump. The curves just illustrate possible states that can be accessed during the passing of the shock wave. A smooth transition would be contradictory to the principles discussed in the preceding paragraphs.

Up to now, the discussion has dealt mostly with the unreacted explosive. It was shown how the CJ-point describes the state of the detonation products for an ideal detonation. The next question is how do we get the information? The Hugoniot is usually estimated using computer codes that estimate detonation products along with equations of state (EOS) (Cooper, 1996). An equation of state for the reaction products is a complex non-linear function of temperature, pressure and density. In the ideal case all of the detonation products will be in the gas phase

which does make the ideal gas law come to mind. Applying this law would however be prone to error due to the high pressures present during a detonation event. The high pressures associated with these events force the molecules to be in contact which is counter to ideal gas behaviour (Johansson and Persson, 1970).

Several equations of state have been applied in attempts to describe the detonation gas. The derivation of which fall beyond the scope of this research, so only the Becker-Kistiakowsky-Wilson equation (BKW-EOS) will be briefly discussed. Equations 2-35 to 2-36 depict the BKW-EOS.

$$\frac{PV}{RT} = 1 + xe^{\beta x} \quad 2-35$$

$$x = \frac{k}{VT^a} \quad 2-36$$

The covolume constant (k) accounts for the residual volume of the gaseous components. Experimental parameters are depicted by a and β . With these equations the detonation pressures can be calculated. It does however have its limitations, in the case of very low temperatures the pressure will become infinitely large. A further development of the BKW-EOS by Cowan and Fickett addressed this problem but brought with it its own limitations (Klapötke, 2012).

2.4 Initiation of detonation

A discussion of the initiation of secondary explosives cannot be done without mentioning hot spot formation. Hot spots are theorised to be responsible for the rapid transition that explosives undergo from initiation to full detonation. These localized points in the bulk material form due to cavities, friction, strains, etc. (Ershov et al., 2013, Akhavan, 2004, Tarver et al., 1996, Handley et al., 2018). In all of the abovementioned cases the result remains the same, that is an increase in localized temperature that exceeds the decomposition and ignition temperatures of the surrounding material, which leads to a rapid acceleration of the reactions leading to a detonation (Ershov et al., 2013).

2.4.1 Shock initiation

In a material undergoing a detonation the decomposition of the material is driven by a shock wave that passes through the material at a speed greater than the speed of sound in the material (Akhavan, 2004, Klapötke, 2012, Cooper, 1996, Johansson and Persson, 1970,

Handley et al., 2018). The pressure at which detonations occur is also considerably higher than those experienced during combustion (Andreev, 1963).

Examples of shock initiation are a detonating primary explosive or an impact by a flying plate. In both cases a shockwave is imparted or generated in the secondary explosive. In order for the shockwave to initiate the detonation event it must exceed minimum energy threshold (Khasainov et al., 2017). This minimum energy barrier is called the critical energy (E_{crit}).

The simplest relation of the minimum energy to the shock wave is for a square wave pulse such as that caused by a flying plate impacting a target medium. The critical energy criterion was originally developed by Walker and Wasley for predicting the response of high explosives to flying plate impact (James, 1988, Yadav, 2006). Critical energy values are available in the literature. They are usually listed as a function of un-shocked density. Equation 2-37 can be used to calculate the impact energy of a flying plate for comparison with literature values (Cooper, 1996, Khasainov et al., 2017, Yadav, 2006).

$$E = Put \quad 2-37$$

The energy (E) transferred by a flying plate is a function of pressure (P), particle velocity behind the shock and shock duration (t). For a flying plate the shock duration is determined by the plate thickness. A modification to Equation 2-37 was suggested by James (1988) to replace the shock duration term with the time of maximum shock (T) energy in the explosive. For a flying plate the values will be identical while for more complex geometries the substitution will provide more accurate values of E_{crit} (James, 1988). Time of maximum shock can be calculated from (Yadav, 2006, James, 1988):

$$T = t = \frac{2d}{U_s} \quad 2-38$$

$$T = \frac{D}{6C} \quad 2-39$$

$$T = \frac{D}{18C} \quad 2-40$$

Equations 2-38 to 2-40 are applicable to flying plates, flat nosed and round nosed rods respectively. For flying plates, Equation 2-38, the time of maximum shock equals to the shock duration. It is a function of plate thickness (d) and shock velocity (U_s) in the plate. For rods, spherical projectiles and shaped charge jets the calculation of the time to maximum shock takes the rod diameter (D), and the velocity of sound in the shocked explosive (C) into account.

The changeover from a plate to a rod occurs for a length to diameter ratio of approximately 1:12 (James, 1988). The pressure amplitude is a function of uncompressed density (ρ_o) of the medium as well as particle velocity and shock velocity as shown in Equation 2-41 or 2-33 (Cooper, 1996)..

$$P = \rho_o u U \quad 2-41$$

Similarly Billingsley and Adams (1994) showed that there may be a critical particle velocity (V_f) which is sufficient to cause crystal lattice fracture, breakup and or disintegration. This minimum particle velocity is called the phonon fission velocity (Billingsley and Adams, 1994). The shock pressure can be calculated by substituting the particle velocity in Equation 2-41 with the critical particle velocity, or phonon velocity as shown in Equation 2-42 (Billingsley and Adams, 1994).

$$P = \rho_o V_f U \quad 2-42$$

Shock wave velocity is calculated by substituting the particle velocity in Equation 2-31 with the critical particle velocity as demonstrated in Equation 2-43 (Cooper, 1996, Billingsley and Adams, 1994).

$$U = C_o + s V_f \quad 2-43$$

Phonon velocity is a function of the limiting free particle velocity (V_l) that can occur without permanent lattice deformation and the mean crystal velocity (C_s) (Billingsley and Adams, 1994). The relation is shown in Equation 2-44.

$$V_f = \frac{V_l + \sqrt{V_l^2 + 4V_l C_s}}{2} \quad 2-44$$

Crystal velocity can be determined by rearranging Equation 2-45 to get Equation 2-46 (Fitzgerald and Wright, 1967). Lattice deformation velocity can be calculated using is shown in Equations 2-47 to 2-49 (Billingsley and Adams, 1994, Fitzgerald and Wright, 1967).

$$DE = m C_s^2 \quad 2-45$$

$$C_s = \sqrt{\frac{DE}{m}} \quad 2-46$$

$$V_l = \frac{h}{2md_l} \quad 2-47$$

$$d_l^3 = \frac{1}{N_v} = \frac{m_{av}}{\rho_o} \quad 2-48$$

$$V_l = \frac{h\rho_o^3}{2m_{av}^{4/3}} \quad 2-49$$

In Equations 2-45 and 2-46 the lattice dissociation energy per atom (DE) and the atomic mass (m) are rearranged in order to isolate C_s . By substituting Equation 2-47 into Equation 2-48 Equation 2-49 is obtained from Equations 2-47 and 2-48 . It relates lattice deformation velocity with Planck's constant (h) and the average weight of a single atom in the material (m_{av}).

The critical energy criterion does not fully describe the complexity of the initiation process as it fails to take into account the release of chemical energy as well as the subsequent growth of the reaction (James, 1988). It has to be used in conjunction with other criteria such as the run to detonation in order to ascertain whether or not detonation will occur. This is because the shock has to travel a certain distance, the run-distance, before steady state detonation is achieved (James, 1988, Cooper, 1996). This distance will vary as it is a function of peak input shock pressure and can be represented on a Pop-plot (Cooper, 1996). The distance required for a steady detonation to occur should be considered when designing an explosive system. The calculations discussed thus far, did not take the particle morphology into account. Particle size and surface area can drastically alter the sensitivity of an explosive to initiation from various stimuli and needs to be considered.

2.4.2 Deflagration to detonation transition (DDT)

Under the right conditions certain granular explosives can undergo a transition from deflagration to detonation. This transition is considerably slower than shock initiation and is initiated by weaker stimuli (Ershov et al., 2013). DDT still requires the formation of a shockwave to drive detonation (Bernecker, 1986, Cooper, 1996, Ershov et al., 2016, Luebcke et al., 1995). The conditions needed for DDT to occur are dependent on confinement, charge diameter charge length, permeability of the packed explosive or density, particle size as well as thermochemical characteristics of the explosive (Cooper, 1996, Bernecker, 1986, Griffiths and Groocock, 1960, Taylor, 1962, Korotkov et al., 1969).

DDT occurs when the rate at which combustion products that are being produced exceeds the rate at which they are removed. The build-up of gaseous combustion products within the system causes an increase in system pressure (Venugopalan, 2015, Andreev, 1963). Confinement drastically improves this build-up by limiting if not entirely preventing losses to the environment. The system can be confined by a shell, tube or the in some cases the explosive material itself can provide sufficient confinement, this however often requires a significant quantity of the explosive material.

It has been shown that the transition is only possible when the combustion process moves from a slow conductive mode of heat transfer to a fast convective mode (Bernecker, 1986, Griffiths and Grocock, 1960, Ershov et al., 2016). This indicates that the energetic medium should have a porous structure in order for the heated gasses to penetrate. The shift from a conductive burning regime to a convective burning regime occurs above a certain critical pressure (Taylor, 1962). Before this point is reached a molten layer of the explosive material provides an effective barrier to gas permeation of the bulk (Taylor, 1962). Without this penetration of the bulk material heat transfer via convection would not be possible. For this reason, lower bulk densities are preferable as it provides more potential pathways for gasses to take as well as limits the thickness of the molten layer by distributing it over larger areas (Taylor, 1962). As density is increased, and as it approaches the theoretical maximum density of the material, the likelihood of DDT occurring decreases significantly (Dai et al., 2014, Luebcke et al., 1995, Luebcke et al., 1996).

The transition from conductive to convective heat transfer is key to DDT as it forces an acceleration in the combustion front. This acceleration in the combustion front increases the rate at which combustion products are produced which in turn increases pressurisation rate (Andreev, 1963). This pressurisation of the system leads to compressive burning. In this state the unreacted material ahead of the burn front is compressed.

Compression leads to a decrease in permeability causing piston like behaviour within the tube (Sáenz and Stewart, 2008, Ershov et al., 2016, Luebcke et al., 1995). This “piston” has a section containing expanding gasses separated from the rest of the explosive material by an impermeable “plug”. This plug forms close to the point of ignition indicating that the rapid convective burning window is relatively narrow (Bernecker and Price, 1974b). The distance at which the plug forms from the ignition point is determined by the autocatalytic nature of decomposition (Luebcke et al., 1995). The plug is driven forwards by rapidly expanding gasses thereby providing the necessary shock to initiate detonation (Sáenz and Stewart, 2008, Luebcke et al., 1995).

The importance of compressive combustion was demonstrated by Luebcke et al. (1996). They placed barriers within a granular PETN column in order to prevent gas permeation into the column beyond a certain depth. Two types of barriers were used, the first was a free moving plug and the second was a fixed plate. In both cases a transition to detonation occurred. In the case of the fixed barrier the pressure rise in the reaction zone caused it to shear free from the surrounding walls forcing it into the adjacent material similar to the free moving plug. This caused rapid compression of the PETN leading to detonation (Luebcke et al., 1996). This showed that fast convective burning was only important in the initial stages of DDT and demonstrated the requirement for rapid compression and shock formation in order to initiate a detonation.

Most DDT research utilised tubes constructed from various materials. The choice was dependent on the level of confinement required for the explosive being investigated (Luebcke et al., 1995, Luebcke et al., 1996, Ershov et al., 2013, Bernecker and Price, 1974b, Bernecker and Price, 1974a, Griffiths and Grocock, 1960). The tube should be thick enough to contain the pressure rise inside (Bernecker, 1986). It is possible to reduce the level of confinement required by accelerating the transition to detonation (Ershov et al., 2016).

2.4.2.1 Factors to consider

The initial undisturbed explosives density is an important factor for all initiation types. Reliable initiation of the bed, requires a compression rate sufficient to produce a shockwave ahead of the combustion front. Densifying the unreacted region by the compression wave can, however, be inhibitive. This is because the penetration of the combustion products is crucial for the transition to occur. The increased packing density decreases the permeability of the material to the combustion gasses thereby reducing the combustion rate (Andreev, 1963, Bernecker, 1986, Tarver et al., 1996). For this reason, the pressure rise should proceed at a sufficiently high rate to generate the shock required before compaction of the surrounding medium can occur. If not, the density increase caused by this compression will shift the detonation threshold. Recalling Equations 2-37 to 2-42 it is easy to see that an increase in density will increase the critical energy required to initiate detonation. Thereby it decreases the likelihood of the transition occurring.

Combustion of the explosive material can be accelerated by decreasing the particle size (Andreev, 1963). Explosive combustion rate is sensitive to changes in density. A particle size distribution that allows for dense packing will prevent penetration of the bed by the combustion gasses thereby limiting the combustion rate. Andreev (1963) reported a change

in density of $1.7 \text{ g}\cdot\text{cm}^{-3}$ to $1.8 \text{ g}\cdot\text{cm}^{-3}$ was enough to prevent DDT from occurring in an RDX charge with individual particles in a range of $40 \text{ }\mu\text{m}$ to $60 \text{ }\mu\text{m}$. It has been demonstrated that for a particular explosive and particle size distribution there is an ideal density (Griffiths and Grocock, 1960, Luebcke et al., 1996, Sáenz and Stewart, 2008). At densities on either side of the “ideal” the run distance will increase. Ideally particles will be porous grains and of suitable size so as to form a porous bed that allows for facile gas penetration. This will allow rapid heating to cause thermal shock to crack or shatter the grains thereby accelerating the combustion reactions (Andreev, 1963, Taylor, 1962). PETN and RDX are sensitive to thermal shock and have been reported to undergo the transition across a number of particle sizes (Andreev, 1963).

If the ambient temperature is increased to a point at which the explosive material starts to melt but does not yet decompose it can decrease susceptibility to DDT. The susceptibility to DDT is enhanced when the heating induces decomposition in preference to melting. This has been shown to occur with PBX-2. When heated to $85 \text{ }^{\circ}\text{C}$ it was found that the binder would melt and reduce the porosity of the explosive charge (Dai et al., 2014). A similar effect is expected to occur in non-plastic bonded explosives where the explosive melt will block decomposition gasses from penetrating the bulk explosives.

This in turn raises a question about the relationship between the ability to undergo DDT and the temperature at which the energetic material burns. There appear to be a correlation between the combustion temperature and the ease at which DDT occurs for a given explosive. PETN has a calculated combustion temperature, approximately $500 \text{ }^{\circ}\text{C}$ higher than that of Tetryl and more than $1000 \text{ }^{\circ}\text{C}$ higher than that of TNT (Andreev, 1963). Of these explosives PETN undergoes DDT at lower pressures than Tetryl (Andreev, 1963). TNT does not undergo DDT even under extreme confinement (Bernecker and Price, 1974a, Andreev, 1963). The higher temperature of the combustion products assist with accelerating the penetration of the burn front into the bulk material (Andreev, 1963).

Bernecker and Price (1974a) noticed unstable propagation of the convective flame in some explosive materials featuring low combustion rates. This suggest that a too slow combustion rate may make an explosive material unsuitable for DDT. This applies to ammonium picrate ($\text{C}_6\text{H}_6\text{N}_4\text{O}_7$) and TNT while RDX, even as wax mixture, does undergo DDT readily (Bernecker and Price, 1974a, Bernecker and Price, 1974b). A further connection is that materials that are sensitive to shock initiation are also be more likely to undergo DDT (Bernecker and Price, 1974b). This makes sense as the DDT transition requires the presence of a shock wave.

The charge diameter affects velocity at which the burn front travels (Luk'yanchikov et al., 2010). There is a critical diameter below which DDT will not occur (Luk'yanchikov et al., 2010). The critical diameter for an explosive is the diameter below which a steady-state detonation cannot be maintained (Cooper, 1996). This diameter is strongly affected by the factors discussed thus far (Cooper, 1996)

The manner in which the deflagration is initiated can also play a big role in the speed of the transition. It has been shown that DDT can be accelerated by utilising a high temperature gas flow to ignite a packed bed of high explosives (Ershov et al., 2016).

2.4.2.2 Accelerated DDT

The stages of the DDT can be summarised as follows (Bernecker, 1986, Ershov et al., 2016, Luebcke et al., 1995, Grigor'ev et al., 2001, Ershov et al., 2015):

1. Pre-ignition;
2. Ignition and conductive burning;
3. Convective burning;
4. Hot spot formation;
5. Compressive burning, and
6. Detonation.

The accelerated DDT, mentioned earlier, resulted from an immediate jump to convective burning (Ershov et al., 2013, Ershov et al., 2015). This avoided the much slower conductive burning stage thereby accelerating the transition considerably. The high enthalpy gas used in that investigation (Ershov et al., 2013, Ershov et al., 2015) was provided by a donor high explosive charge that was separated from the acceptor by an air gap. Pressure measurements indicated that the initial detonation produced a shock significantly lower than that required to initiate the acceptor charge. This is similar to the rapid transition to detonation documented by Grigor'ev et al. (2001) when initiating a porous high explosive with the detonation products of a gas mixture.

The elevated pressure at which the gas was provided increased the combustion rate of the explosive material (Andreev, 1963, Ershov et al., 2016, Luk'yanchikov et al., 2010). The transition to detonation occurred within 10 μ s, this is a significant reduction in the time it usually takes to undergo the transition when using other techniques (Ershov et al., 2013, Ershov et al., 2015, Ershov et al., 2016). By making the jump directly to the accelerated burning the entire slow deflagration stage was avoided which has been reported to be around 20 μ s for PETN (Luebcke et al., 1996).

The premise behind this increased burn rate can potentially be explained by the fact that the linear burn rate described by Equation 2-11 does not accurately describe porous fuel grains (the explosive in this case) as seen with porous or foamed propellants (Eisenreich et al., 2002). Higher mass conversion rates can be obtained due to the penetrating effect of the hot decomposition gasses which leads to hot spots forming in the pores drastically increasing the overall burning surface. Extending this to the preceding example the hot pressurised gasses provided can initiate hot spot formation due to its ability to penetrate both the porous body of the explosive as well as any potential pores in the explosive grains themselves. This significantly increases the mass burn rate. The mass burn rate is therefore a function of the total burning surface area of the explosive and not just the cross sectional area (Eisenreich et al., 2002).

Comet et al. (2015) illustrated a method to produce a primary explosive free initiating device using an energetic nano-composite. In the method they used, aluminium-based nano-thermites mixed with nano-RDX. The composition had an RDX content of 60 wt. %. This system was capable of undergoing DDT within 20 mm of the ignition point. The detonation was of sufficient force to initiate adjacent PETN pellets. The addition of the nano-thermite was necessary in order to accelerate the transition to detonation. Comet et al. (2015) reported a run distance of approximately 30 mm for RDX without the addition of the thermite. Furthermore, it was reported that the transition could be achieved in a shorter distance when using an RDX loading approximately 40 wt. % or 80 wt. %. Both these achieved a detonation within 10 mm of the initiation zone. The shorter distance required for the transition was reasoned to be due to the ability of the thermite to propagate the combustion reaction down the column. This means that the thermite was assisting in the initial two stages of DDT as listed.

What should be apparent by this stage is that DDT is not a simple mechanism for initiating a detonation. In order to simplify the calculation while trying to replicate experimental designs most DDT models encountered are one-dimensional. The model needs to account for the following:

- Momentum, mass and energy balances;
- Ignition criteria;
- Equations of state, and
- Compaction equations.

It was found that traditional ignition theories do not accurately predict the time to ignition of unreacted explosive particles when attempting to model accelerated DDT (Ershov et al., 2013, Ershov et al., 2015, Ershov et al., 2016). This was attributed to the complexities arising from the short run times associated with this form of initiation.

2.5 Initiators

An explosive or ignition train is an assembly of combustible and or explosive components arranged from the most sensitive to the least sensitive (VA, 1974, Carlucci and Jacobson, 2008). Explosive trains are used to initiate a detonation event in a controlled manner while an ignition train is typically used to initiate combustion of a propellant. An ignition or low explosive train usually consists of primary charge and a gas generating charge (VA, 1974). The primary charge can take the form of a primer or an ignition charge. A delay charge may also be included depending on the application (VA, 1974).

A high explosive train is more complex than the low explosive train. It generally consists of the following parts (VA, 1974):

- A low explosive charge. This charge is contained within a suitable housing. It provides a thermal and a pressure output.
- This is followed by the intermediate charge, which is a primary explosive. A rapid transition to detonation occurs in this section.
- A secondary explosive follows the primary explosive. This charge boosts the output of the primary explosive and initiates the main charge.

The elements listed are usually accompanied by further auxiliary components such as delay elements, relays and booster charges to assist in initiating insensitive main charges (VA, 1974). Initiation systems vary in design and working principle depending on the application. The brief summary that follows will broadly group the initiators as electrical and non-electrical.

2.5.1 Nonelectric initiators

Nonelectric initiators can be classified as flame or spark, friction, stab and percussion (Cooper, 1996). The output and therefore the intended application differs for these categories. A match exemplifies friction initiation. Detonators are usually flame or spark initiated while cartridge primers rely on percussion (Cooper, 1996).

2.5.1.1 Detonator

A detonator contains multiple parts of the high explosive train. The detonator is considered one of the most important inventions in the field of energetic materials (Ziegler, 1987). Alfred Nobel invented the detonator consisting of a metal capsule containing mercury fulminate 1865 (Johansson and Persson, 1970). The presence of a primary explosive demonstrates the initial insight into the importance of a shock wave for initiation. It superseded the black powder based thermal igniter invented two years earlier (Johansson and Persson, 1970). Without detonators safe and controlled blasting operations would not be possible. The basic construction of a nonelectric detonator is depicted by Figure 2-5.

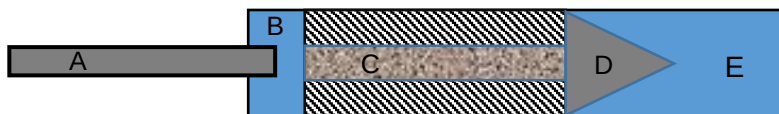


Figure 2-5. Nonelectric pyrotechnic delay detonator modified from (Ziegler, 1987).

The basic diagram in Figure 2-5 depicts a non-electric detonator. Detonators of differing designs will still share certain similarities. Figure 2-5 (A) shows a shock tube which transfers a “signal” to the detonator. Depending on the type of detonator the input signal will differ. Electrical detonators will receive an electrical current whereas in the example shown the signal transmitted by the shock tube will be a deflagration wave. The outer casing of the detonator (B) protects the internal components from environmental exposure. The pyrotechnic delay element is housed within the tube (C). The delay element burns at a specific rate allowing control of the detonation sequence. In the case of an electrical detonator the pyrotechnic delay element can be replaced by a delay circuit connected to a fuse head. The primary explosive charge (D) follows the delay. It initiates the detonation event in the base charge (E). The base charge provides the detonator “output”.

2.5.1.2 Percussion primers

Percussion primers used in ammunition are used to initiate combustion of the propellant. Two major categories exist, rim-fired or centre fired (Cooper, 1996). In either case the composition is initiated by impact. Impact squeezes the composition between the outer cup and the anvil (Oyler et al., 2015, Cooper, 1996). The main goal of the ignition system is to provide rapid ignition of the propellant (Carlucci and Jacobson, 2008). Furthermore, this ignition should be achieved in a “smooth” manner, as in pressure spikes should be avoided as it can crush propellant grains thereby altering the combustion performance (Carlucci and Jacobson, 2008). Primer compositions can be broken down into the following components (Oyler et al., 2015):

- Primary explosive;
- Sensitizer;
- Oxidiser;
- Fuel, and
- Binder.

A primary explosive is used to receive the “signal” then provide a rapid response in the form of heat and pressure (Oyler et al., 2015). Lead styphnate is a commonly used primary explosive in these primers. It is however not sensitive enough for standard applications. For this reason sensitizers are added, e.g. tetrazene or ground glass (Oyler et al., 2015). The fuel and oxidiser components increase the heat and slag output. This allows for smooth ignition of the propellant (Oyler et al., 2015).

2.5.2 Electric initiators

Detonators were originally initiated by a safety fuse. In an effort to increase reliability and safety, a move was made to electric firing systems (Ziegler, 1987). Electric systems use an electric spark to initiate the primary explosive (Ziegler, 1987). Spark detonators reduce the risk of unintended detonations due to stray currents (Ziegler, 1987). These developments were however unsafe in environments where methane was present. Further development lead to the first bridge wire detonators. These detonators use a hotwire to ignite a flash composition which in turn triggers the primary explosive (Ziegler, 1987).

Production and handling of primary explosives remains a concern. The first detonator to avoid the use of primary explosives was the exploding bridge wire (EBW) detonator (Varosh, 1996). It was developed in in the 1940's as part of the Manhattan project but only patented in 1962 after it was declassified (Varosh, 1996, Rae and Dickson, 2019). EBW has components similar to electric detonators (Ziegler, 1987). Instead of a primary explosive it utilises a secondary explosive that is pressed into layers with varying density (Ziegler, 1987). The explosive in contact with the bridge wire is usually at 50 % the crystal density (Varosh, 1996, Rae and Dickson, 2019). Applying sufficient current to the bridge wire causes it to heat at a rate far exceeding its thermal expansion ability leading to an explosion (Varosh, 1996). This explosion produces a shockwave which triggers the detonation of the secondary explosive (Varosh, 1996, Ziegler, 1987).

A related detonator development is that of the exploding foil initiator (EFI). EFI's otherwise known as slappers were invented in 1965 (Varosh, 1996). These systems are similar to EBW

initiators in that they are electrical and contain no primary explosives. The initiators however differ from the EBW type by using a “projectile” impact to shock the secondary explosives (Varosh, 1996, Ziegler, 1987, Brown et al., 2017). They work by providing current to a bridge film which explodes. This explosion drives a dielectric flyer down a barrel into the secondary explosive pellet (Varosh, 1996, Fousson et al., 2016).

Another iteration of the primary explosive free-electric detonator shares similarities with both preceding examples. The flying plate detonator (FPD) was developed by the Bureau of Mines (Ziegler, 1987). The FPD consists of a combustion chamber and a barrel that is separated by a sealing or confining plate. It uses an EBW to ignite a highly compressed donor charge situated in the combustion chamber (Held, 1996). The combustion of the donor charge leads pressurises the combustion chamber. The projectile, flying plate, is formed from the confining plate. This happens when the pressure in the combustion chamber exceeds the mechanical limits of the confining plate, thereby shearing free the “projectile”. The projectile formed in this process is accelerated towards the acceptor charge at the end of the barrel (Held, 1996, Ziegler, 1987). The pressure at which the fly plate shears is in the range of 350 MPa to 450 MPa (Held, 1996). The acceptor charge is initiated by the shock induced by the impact of the high velocity plate. A variation on this design uses a capacitor to heat the initial explosive charge instead of an EBW (Fousson et al., 2016).

For both the EFI and FPD initiation of the detonation event is by means of an imparted shock wave due to the impact of the projectile on the acceptor charge. The reliability of the detonators is therefore related to the velocity attained by the projectile (Fousson et al., 2016). Projectile velocity is dependent on a multitude of factors including but not limited to the confinement of the initial combustion process, projectile mass, thickness of the projectile and the shear thickness (Fousson et al., 2016, Glavier et al., 2017).

The discussion thus far has shown that the electric detonator can be divided into two classes. The first being those that contain primary explosives and a second that doesn't. The construction of the second class is more complex and expensive than the electrical methods discussed earlier (Varosh, 1996). They do however offer benefits including safety, reliability and repeatability (Varosh, 1996, Ziegler, 1987, Held, 1996). That is why they see use in certain applications.

2.5.3 Projectile-based detonator ballistics

The projectile-based initiators discussed in the chapter share features with those of a simple gun. A propellant is used to accelerate a projectile down a tube or barrel. For this reason, a basic understanding of ballistics can assist with the development of an appropriate design. Ballistics can be broken down into the following categories: internal, transitional, external and terminal. Internal ballistic calculations describe the projectile motion during the initial powered part of its flight. The transitional region describes the complex crossover between the muzzle of the launch device and the external ballistic region. External ballistics is the unpowered part of the projectile flight up to the point of impact at which point terminal ballistic calculations will be used. The categories are illustrated in Figure 2-6.

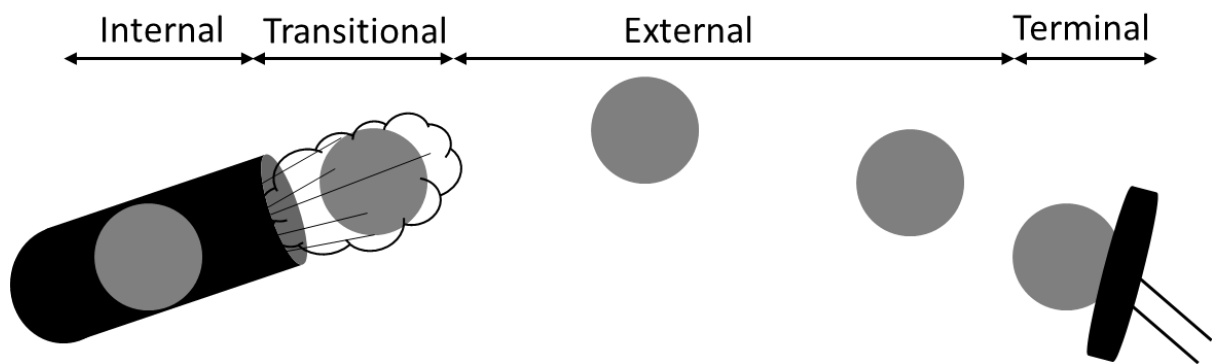


Figure 2-6. Ballistic breakdown for a projectile.

In the case of FPD the scheme will be somewhat different from that depicted in Figure 2-6, due to the fact that the barrel is in contact with the target. This means that the projectile should not experience the intermediate or external sections of the flight path shown in Figure 2-6.

2.5.3.1 Internal ballistics

There are several counteracting forces acting on the projectile while it is in the barrel. The Driving force moving the projectile towards the muzzle is the expanding combustion gasses of the propellant. The projectile will only accelerate should the force be able to overcome friction and the force exerted by the atmosphere ahead of it (Jiang, 2003). In order to model the projectile as it moves down the barrel the following equations are necessary (Baer and Frankle, 1962):

- Energy equation;
- Equation of state;
- Burning rate equations; and
- Equations of projectile motion.

These equations will be discussed as they appear in (Baer and Frankle, 1962) Applying the law of conservation of energy to a projectile being fired from a gun results in Equation 2-50

$$Q = U + W + Losses \quad 2-50$$

The energy released by the burning propellant (Q) is equal to the sum of the internal energy of the propellant gasses (U), external work done on the projectile (W) and the secondary energy losses.

The energy released by a propellant mixture is assumed to be equal to the sum of the energy released by the individual propellants. The internal energy of the propellant gas is calculated in a similar manner. See Equation 2-51 and 2-52 (Baer and Frankle, 1962).

$$Q = \sum_{i=1}^n [C_i Z_i \int_0^{T_{o_i}} C_{v_i} dT] \quad 2-51$$

$$U = \sum_{i=1}^n [C_i Z_i \int_0^T C_{v_i} dT] \quad 2-52$$

The initial mass of a propellant (C_i) and the fraction burnt (Z_i) are necessary for both equations. The adiabatic flame temperature (T_{o_i}) is higher than the gas temperature (T) due to expansion and work performed (Baer and Frankle, 1962). The work done on the projectile is a function of the projectile base area (A), the pressure at the base (P_b) and the displacement of the projectile (x). It is shown in Equation 2-53.

$$W = A \int_0^x P_b dx \quad 2-53$$

Assuming that the specific heat capacity remains constant between the adiabatic combustion and gas temperatures the mean can be used ($\bar{C}_{v_i}$). Substituting Equations 2-51, 2-52 and 2-53, into Equation 2-50 results in Equation 2-54 with some rearrangement and integration.

$$\sum_{i=1}^n [C_i Z_i \bar{C}_{v_i} (T_{o_i} - T)] = A \int_0^x P_b dx + losses \quad 2-54$$

Equation 2-542-54 can be solved for the gas temperature as shown in Equation 2-55.

$$T = \frac{\sum_{i=1}^n C_i Z_i \bar{C}_{v_i} T_{o_i} - (A \int_0^x P_b dx + losses)}{\sum_{i=1}^n C_i Z_i \bar{C}_{v_i}} \quad 2-55$$

The force (F_i) provided by each propellant in the mix is defined by Equation 2-56 as a function of its specific mass (m_i) and adiabatic combustion temperature (Baer and Frankle, 1962).

$$F_i = m_i R T_{o_i} \quad 2-56$$

Equation 2-56 can be rearranged and written in terms of the specific heat ratio (γ_i) and the specific heat at constant volume. This is shown in Equation 2-57 to Equation 2-60

$$\overline{C_{p_i}} - \overline{C_{v_i}} = m_i R \quad 2-57$$

$$\gamma_i = \frac{\overline{C_{p_i}}}{\overline{C_{v_i}}} \quad 2-58$$

$$\overline{C_{v_i}}(\gamma_i - 1) = m_i R \quad 2-59$$

$$T_{o_i} = \frac{F_i}{\overline{C_{v_i}}(\gamma_i - 1)} \quad 2-60$$

The resulting Equation 2-60 can then be substituted into Equation 2-55 to yield Equation 2-61. Baer and Frankle (1962) states that in most instances it can be assumed that the igniter has fully burned, $Z_I = 1$ which allows for Equation 2-61 to be modified to Equation 2-62, where the subscript (I) indicates terms for the ignitor.

$$T = \frac{\sum_{i=1}^n \frac{[C_i Z_i F_i]}{(\gamma_i - 1)} - A \int_0^x P_b dx - losses}{\sum_{i=1}^n \frac{[C_i Z_i F_i]}{(\gamma_i - 1) T_{o_i}}} \quad 2-61$$

$$T = \frac{\sum_{i=1}^n \frac{[C_i Z_i F_i]}{(\gamma_i - 1)} + \frac{C_I F_I}{(\gamma_I - 1)} - A \int_0^x P_b dx - losses}{\sum_{i=1}^n \frac{[C_i Z_i F_i]}{(\gamma_i - 1) T_{o_i}} + \frac{C_I F_I}{(\gamma_I - 1) T_{o_I}}} \quad 2-62$$

The work done on the projectile results in a gain in kinetic energy of the projectile as shown by Equation 2-63

$$A \int_0^x P_b dx = \frac{1}{2} m v^2 = \frac{w_p}{2g} v^2 \quad 2-63$$

The energy losses include (Baer and Frankle, 1962):

- Kinetic energy of propellant gas and unburnt propellant, (E_p) Equation 2-64 ;
- Heat loss to the gun, (E_h); and
- Energy losses resulting from engraving of the rotating band, friction and acceleration of air ahead of projectile, (E_{p_r}) see Equation 2-65.

Taking the losses into account yields Equation 2-66.

$$E_p = \frac{(\sum_{i=1}^n c_i)v^2}{2g\delta} \quad 2-64$$

$$E_{p_r} = A \int_0^x P_r dx \quad 2-65$$

$$T = \frac{\sum_{i=1}^n \frac{[C_i Z_i F_i]}{(\gamma_i - 1)} + \frac{C_I F_I}{(\gamma_I - 1)} - \frac{v^2}{2g} \left(w_p + \sum_{i=1}^n \frac{c_i}{\delta} \right) - A \int_0^x P_r dx - E_h}{\sum_{i=1}^n \frac{[C_i Z_i F_i]}{(\gamma_i - 1)T_{oi}} + \frac{C_I F_I}{(\gamma_I - 1)T_{oi}}} \quad 2-66$$

The energy equation described allows for the calculation of the temperature of the combustion gas. This can then be used with the equation of state in order to calculate the pressure at the base of the projectile which is needed in order to determine its velocity. The mass fraction burning rate equation is necessary in order to determine the rate at which propellant gas is produced, Equation 2-67.

$$\frac{dZ_i}{dt} = \frac{S_i r_i}{V_{g_i}} \quad 2-67$$

$$S_i = f(Z_i) \quad 2-68$$

The linear burn rate (r_i) in Equation 2-67 is equal to Equation 2-11 for most propellants (Baer and Frankle, 1962). The surface area (S_i) of the partially burn propellant is a function of the mass fraction of the burnt propellant as shown in Equation 2-68.

The forces acting on the projectile in the axial direction are (Baer and Frankle, 1962) :

- Propulsive force (F_p), Equation 2-69;
- Frictional force (F_f), Equation 2-70; and
- Retardation force (F_r), Equation 2-71.

The directions of the forces are indicated in Figure 2-7.

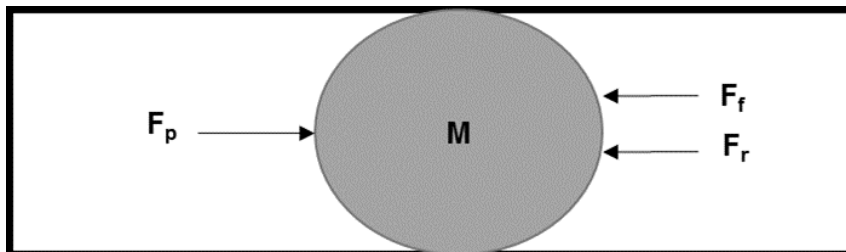


Figure 2-7. Simplified depiction of the forces acting on a projectile while it's in the barrel.

$$F_p = P_b A \quad 2-69$$

$$F_f = P_r A \quad 2-70$$

$$F_r = P_g A \quad 2-71$$

The pressures required in Equation 2-69 to 2-71 are the pressure at the base of the projectile (P_b), resistance pressure and the pressure of the gas ahead of the projectile (P_g). The resultant force is calculated using Equation 2-72 or 2-73.

$$F_a = F_p - F_f - F_r \quad 2-72$$

$$F_a = A(P_p - P_f - P_r) \quad 2-73$$

The acceleration of the projectile can be calculated using the resultant force and the projectile mass 2-74 (Lemley et al., 1971, Baer and Frankle, 1962).

$$a = \frac{F_a}{M} \quad 2-74$$

Velocity and displacement are calculated using Equations 2-75 and 2-76.

$$v = \int_0^t a \, dt \quad 2-75$$

$$x = \int_0^t v \, dt \quad 2-76$$

If the acceleration is known and assumed to be constant over the extent of the barrel, the time spent in the barrel by the projectile and its final velocity can be calculated from Equations 2-77 and 2-78 (Lemley et al., 1971).

$$t = \sqrt{\frac{2s}{a}} \quad 2-77$$

$$v = at \quad 2-78$$

In the application, the barrel ends at the target, effectively sealing it off. The compression of the gas trapped there as the projectile moves towards the target will resist its motion. Figure 2-8 depicts the target explosive affixed to the barrel of the FPD element.

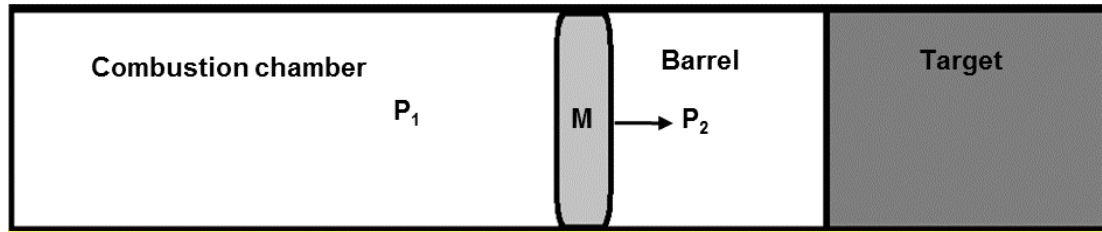


Figure 2-8. Depiction of the FPD system, with the barrel directly against the target.

If it is assumed that there is no heat transfer to the environment or between the combustion chamber and that the barrel is perfectly sealed. Then the barrel temperature will only be a function of compression. The chamber volume is determined by the position of the projectile. The change in temperature can be calculated with Equation 2-79 (Carlucci and Jacobson, 2008):

$$T = T_i \left(\frac{V_i}{V} \right)^{\gamma-1} \quad 2-79$$

In Equation 2-79 the subscript (*i*) indicates the initial state. The symbol γ represent the ratio the specific heats. In this instance the retardation force will increase due to the rise in pressure ahead of the projectile. An increase in the retardation force will decrease the velocity of the projectile, see Equations 2-72 to 2-75. The sharp pressure rise in front of the projectile may in fact also assist in initiation of detonation. John (1981) has shown that the rapid compression of a gas layer adjacent to a high explosive can ignite a high explosive similar to the rapid transitions from deflagration to detonation discussed in Section 2.4.2.2.

2.5.3.2 Transitional and external ballistics

Since the general design of a FPD does not allow for eternal unpowered flight the transitional and external aspect of ballistics will only be discussed briefly. During the transition from internal to external ballistic motion the projectile will still experience some “push” from the propellant gas (Cayzac et al., 2011, Yu and Zhang, 2010). This means that the maximum velocity is actually achieved at some distance away from the barrel due to the propellant gasses still driving the projectile during the transitional stage (Yu and Zhang, 2010). Jiang (2003) characterised the process of a supersonic projectile leaving a barrel with, two blast waves and jet flows, and a bow shockwave. As mentioned in Chapter 2.5.3.1, a projectile traveling down a barrel acts like a piston. When the projectile is traveling at supersonic speeds it drives a precursor shockwave ahead of it (Yu and Zhang, 2010, Jiang, 2003). When this wave escapes the barrel a blast develops (Yu and Zhang, 2010, Jiang, 2003). The projectile that is leaving the barrel will interact with the diffraction waves and jet flow produced by the

preceding shock (Jiang, 2003). This is followed by a second blast shortly afterwards. The second blast is caused by the propellant gas expanding out of the barrel behind the projectile (Jiang, 2003). The second blast overtakes the projectile initially, but it and the preceding shock will be overtaken by the projectile at some distance from the barrel (Yu and Zhang, 2010, Jiang, 2003). The process described can affect both the maximum velocity and accuracy of the projectile.

A projectile in flight is under the influence of a number of forces such as, drag, lift and gravity (Allen, 2018, Carlucci and Jacobson, 2008). These forces affect the trajectory, accuracy of the projectile flight (Allen, 2018, Carlucci and Jacobson, 2008). Drag force effects will be briefly discussed considering spherical projectiles of varying diameter but of fixed density of $11.3 \text{ g}\cdot\text{cm}^{-3}$. The projectiles are fired at a flat trajectory. Using the model of Allen (2018) the effect the projectile diameter is illustrated in Figure 2-9.

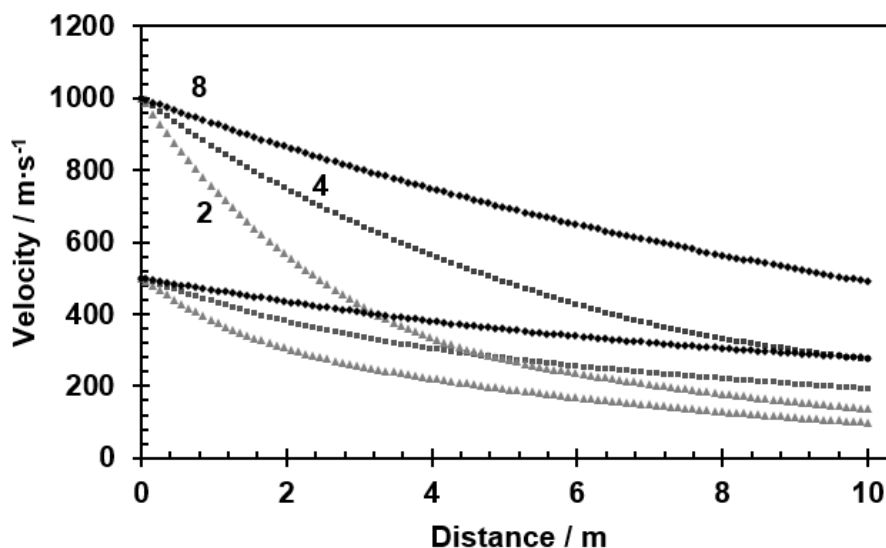


Figure 2-9. Projectile velocity change over distance for projectiles of 8 mm, 4mm and 2 mm in diameter with initial velocities of $500 \text{ m}\cdot\text{s}^{-1}$ and $1000 \text{ m}\cdot\text{s}^{-1}$.

The drag force experienced by the projectile is a function of its velocity and its diameter (Allen, 2018, Carlucci and Jacobson, 2008). The velocities in Figure 2-9 show that a larger projectile maintains its velocity better. It is also clear that the initial velocity plays a big role in the rate of deceleration. All three projectile diameters demonstrated significant deceleration when the initial velocity was $1000 \text{ m}\cdot\text{s}^{-1}$ compared to $500 \text{ m}\cdot\text{s}^{-1}$. The first occurrence can be explained by the greater momentum of the larger projectiles due to higher mass. This requires a greater force to overcome than for a lighter projectile. The larger projectile does however have a larger cross-section which will increase the drag force it experiences. This force is also the reason

for the comparatively rapid decrease in in velocity witnessed for the projectiles starting at a velocity of $1000 \text{ m}\cdot\text{s}^{-1}$. The drag force experienced by the spherical projectiles in Figure 2-9 can be described with Equation 2-80 (Allen, 2018).

$$F = \frac{\pi D^2 \rho_a v^2 C(M, Re)}{8} \quad 2-80$$

The drag force is a function of both the projectile and atmospheric properties, like projectile diameter (D), velocity (v), and drag coefficient ($C(M, Re)$) air density (ρ_a). The drag coefficient is function of the Reynolds (Re) and the Mach (M) numbers the calculation of which can be seen in Equations 2-81 and 2-82 (Allen, 2018).

$$M = \frac{v}{v_s} \quad 2-81$$

$$Re = \frac{D \rho_a v}{\mu_a} \quad 2-82$$

In Equations 2-81 and 2-82 the speed of sound in air is indicated by (v_s) and the air viscosity is given by (μ_a). Allen (2018) calculated the drag force with the following set of linear Equations:

$$C(M) = 0.92 + 0.0375M \text{ for } 1.2 \leq M < 2.0 \quad 2-83$$

$$C(M) = -0.163 + 0.94M \text{ for } 0.7 \leq M < 1.2 \quad 2-84$$

$$C(M) = 0.418 + 0.110M \text{ for } 0.02 < M < 0.7 \quad 2-85$$

The equations were derived by fitting the straight lines to drag coefficient and Mach number data for a Reynolds number of 10000 (Allen, 2018).

2.5.3.3 Impact needed

The basic principles shock initiation have been discussed in Chapter 2.4.1. In order to initiate the target explosive the projectile impact needs to impart a minimum level of energy to initiate the detonation, see Equation 2-37. This energy is dependent on the type of explosive used and its packing density.

If the projectile dimensions and material properties are known, and the projectile is shot at a known velocity at an explosive the first step would be to calculate the interface pressure between the projectile and the target. In order to do this we look at the P-u Hugoniot as described in Chapter 2.3. The interface pressure between the flyer and the target is the same one which allows one to equate the two Hugoniot equations. The resulting equation can be

solved for particle velocity. With this velocity known, the interface pressure can be determined by substituting the velocity back into any of the two Hugoniot equations. Thereafter, the shock velocity in each material can be calculated from Equation 2-31.

The required shock duration is given by Equation 2-37. This can be determined by calculating the time the shock wave takes to reach the back of the projectile and for the subsequent rarefaction wave to return and reach to interface again. The energy imparted by this impact can then be calculated with either Equation 2-37 or 2-86 (Cooper, 1996, Souers and Vitello, 2007).

$$E = \frac{P^2 t}{\rho U} \quad 2-86$$

Should it exceed the critical energy required for a detonation, Pop-plots can be considered to determine what the run distance to detonation would be. PETN was used for the following simulations. A density of $1600 \text{ kg}\cdot\text{m}^{-3}$ was used. The steel flyer selected was a plate with a thickness of 4 mm. Impact velocity was varied between $0.1 \text{ km}\cdot\text{s}^{-1}$ and $3 \text{ km}\cdot\text{s}^{-1}$. The results of the simulations are shown in Figure 2-10.

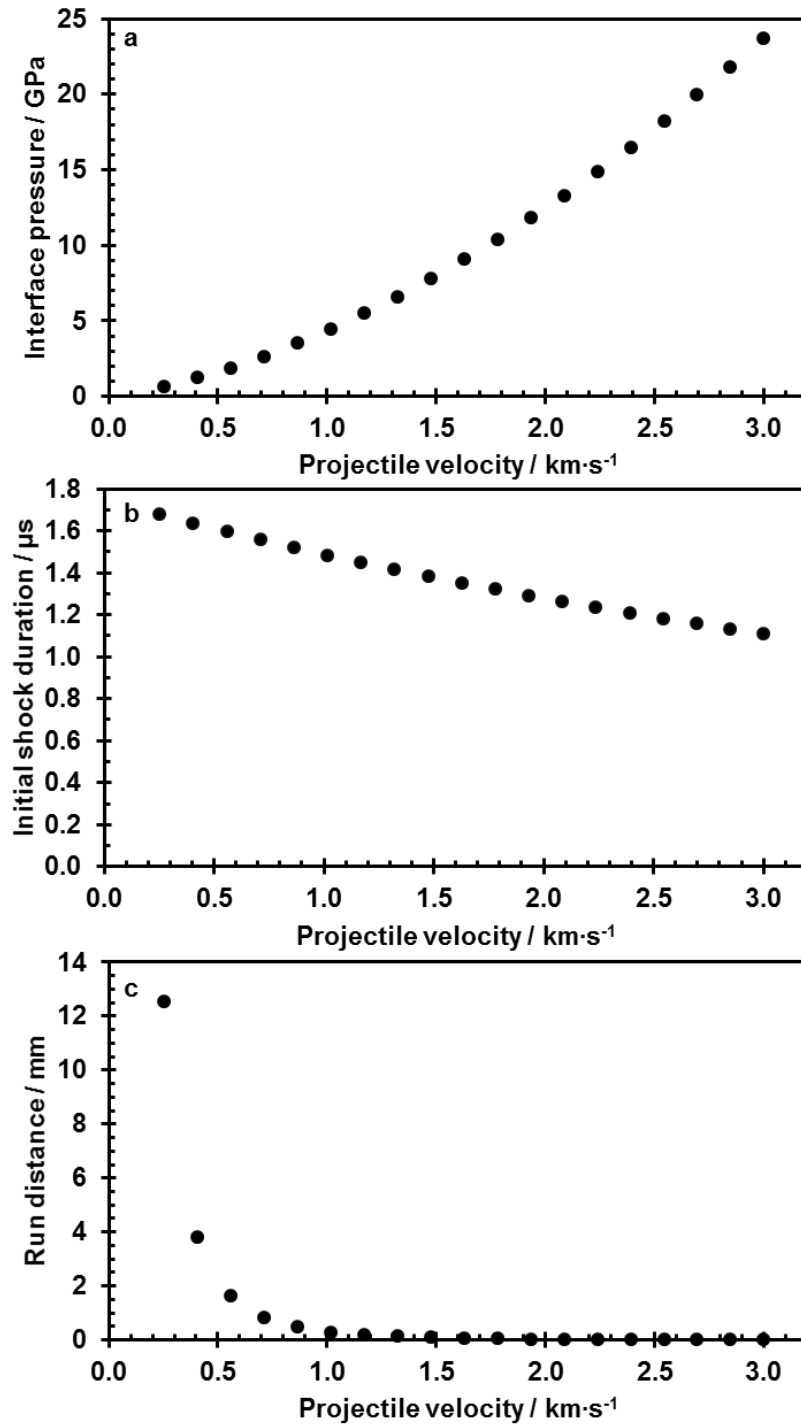


Figure 2-10.(a) Interface pressure, (b) initial shock duration and (c) distance to detonation as a function of initial projectile velocity.

The results shown in Figure 2-10 illustrate the procedure that can be used to determine whether or not the initial projectile velocity is within a range sufficient to initiate a detonation. All the velocities, shown in the preceding Figure, exceeded the required for the critical energy to be exceeded. The run distance, for the various velocities is shown in Figure 2-10 (c), were

calculated using the Pop-plot data from Cooper (1996). The pressure range was, however, limited to within the 1.2 GPa - 2 GPa range. This range limits the calculations to an initial projectile velocity of approximately $0.6 \text{ km}\cdot\text{s}^{-1}$. Alternatively, Stirpe et al. (1970) provides data for a larger pressure range as shown in Figure 2-11.

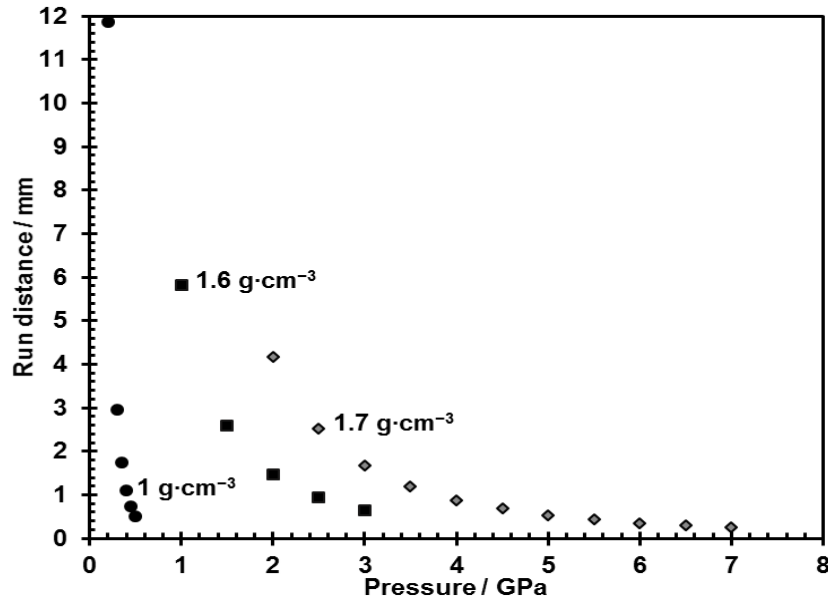


Figure 2-11. Pop-plots for PETN at different initial densities, data adapted from Stirpe et al. (1970).

The next steps would be to determine if the pulse duration and magnitude are sufficient, as well as look at the shock diameter (Cooper, 1996). For a shock to initiate detonation it is required that it maintains its peak pressure in the explosive for at least the ideal run distance described by the Pop-plot data. If the pulse is very thin the explosive will not detonate. The pulse duration for a square shockwave formed by flyer impact is shown in Equation 2-87 (Cooper, 1996).

$$t = \frac{x_f}{U_f} + \frac{x_f}{R_f} \quad 2-87$$

In Equation 2-87 the time or shock duration (t) is calculated from the flyer thickness (x_f) and the shock (U_f) and rarefaction (R_f) velocity. The subscript (f) indicates the flyer. The rarefaction wave speed is estimated from Equation 2-88.

$$R = C_0 + 2su \quad 2-88$$

In the same time that the shock has travelled distance (x) the rarefaction will have travelled ($x - x_L$). This is illustrated in Equation 2-89, subscript (HE) indicates the explosive. This Equation indicates the point in time at which the rarefaction has caught up with the shock. Up to this point the shock will maintain peak pressure. The distance can be calculated by combining Equation 2-89 Equation 2-90. Rearrangement gives Equation 2-91. This is the distance over which the shock will maintain a constant peak pressure (Cooper, 1996).

$$\frac{x}{R_{HE}} = \frac{x - x_L}{U_{HE}} \quad 2-89$$

$$x_L = U_{HE}t \quad 2-90$$

$$x = \frac{U_{HE}R_{HE}t}{R_{HE} - U_{HE}} \quad 2-91$$

A good flyer design usually has a diameter which is double the desired run distance (Cooper, 1996). Figure 2-12 depicts the process.

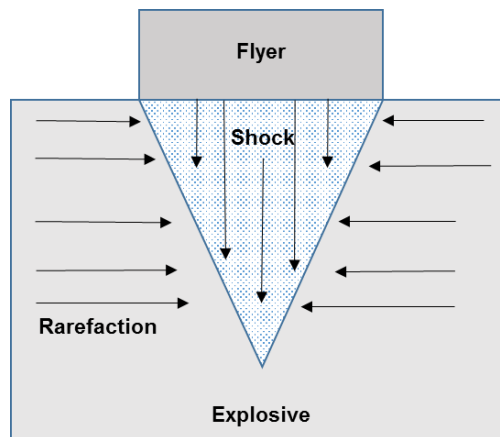


Figure 2-12. Circular flyer impact inducing a shockwave in a target explosive and subsequent interaction with rarefaction waves Cooper (1996).

In Figure 2-12 a circular flyer striking an explosive is illustrated. The impact generates a shockwave. This shock wave travels forward axially into the explosive (Cooper, 1996). Shock pressure is alleviated from the sides by rarefaction waves that propagate radially inward (Cooper, 1996). The rarefaction waves formed at the edges where the shock reached ambient pressures. The effect causes a cone-shaped zone to form. This zone or region is the only area in which the initial shock pressure can endure (Cooper, 1996). This means that for detonation to occur the cone height should be at least as high as the run distance required.

2.5.4 Deflagration to detonation detonators

Initiators exist that solely operate on the principle of DDT. These detonators do have the benefit of avoiding the use of primary explosives, which is beneficial from a safety and environmental standpoint. It should be clear by now that the transition to a full detonation event will be slower and therefore require some design considerations. An example of this is the design of Wuensche et al. (2012) where the deflagration to detonation region is contained within a bulkhead. The bulkhead allows the pressure to be contained until the transition to detonation can occur. Alternatively an initiating element can be used, in this case the DDT event is confined in a reinforced element loaded into a detonator shell (Lindqvist et al., 1995). This element contains the initiating charge and is of a sufficient length to allow the transition to detonation to occur. Another example of a steel element used to confine the system is seen in the patent of (Dumenko, 2001). The patent describes an initiation element containing a pyrotechnic charge that acts as an igniter and to a lesser extent a gas generator. Under the confined conditions found within the ignition element the gas generated by the ignition charge rapidly drives the low density secondary explosive charge into a convective burning state, which can then transition into a detonation.

Another interesting development in this field is that of “new composite” primary explosives. These systems contain a suitable high explosive combined with a thermite (preferably a nano-thermite). The combination of these components leads to the system that burns at an enhanced rate before it transitions to a detonation event (Luo et al., 2018)

The few examples shown all have a method to contain the reaction zone while the pressure rises and develops. A reinforcing sleeve may be the simplest solution for converting components of existing detonators into DDT detonators. While the DDT element, or cartridge, is more complicated to manufacture, it may provide a more effective solution to applications where the external geometry of the detonator is crucial.

2.6 PETN

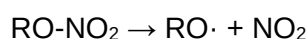
PETN is a nitrate ester widely used in commercial blasting caps and detonation cords. Due to this extensive use it is considered the target explosive for the rest of the study. Its widespread use is owed to relatively low friction sensitivity as well as its thermal stability (Fordham, 1980, Cooper, 1996, Akhavan, 2004). PETN was first prepared by the nitration of pentaerythritol in 1894 (Akhavan, 2004).

relatively slow mass loss which accelerates to reach a maximum at 206 °C coinciding with the peak of the decomposition. In addition to the DTA and TGA analysis Huang et al. (1992) also used a modified manometric stability test (MVST). In these tests the PETN was kept at a fixed temperature in evacuated tubes for 40 hours. During this time, the pressure was recorded at 10 s intervals. The tests conducted by Huang et al. (1992) were done at temperatures of 100 °C, 110 °C and 120 °C, i.e. below the melting point of PETN. The degradation rate might be not phase dependant. Degradation rates can vary for a variety of reasons including the experimental conditions, the presence of moisture, contamination by metal oxides or acid species and the presence of different polymorphs the sample (Foltz and Lawrence Livermore National Laboratory, 2009).

Even in the absence of degradation, sublimation occurs at relatively low temperatures (Gershanik and Zeiri, 2012). In the study by Gershanik and Zeiri (2012) PETN crystals were deposited on a quartz micro balance which continually monitored the change in mass for the duration of the isothermal tests. The mass loss rate in isothermal runs increased 15 fold when the temperature was increased from 50 °C to 70 °C (Gershanik and Zeiri, 2012).

Non-isothermal degradation studies on single PETN crystals yielded an apparent activation energy ranged from 170 kJ·mol⁻¹ to 176 kJ·mol⁻¹ (Bhattacharia et al., 2015, Huang et al., 1992). According to Bhattacharia et al. (2015), the formation of nitrogen dioxide (NO₂) is the rate determining step in the decomposition of PETN according Scheme 2-1.

Scheme 2-1



The fission of the O-NO₂ bond is the primary initiator of degradation under most forms of stimuli (Zeman and Jungová, 2016). This process produces an alkoxy (RO·) radical as well as nitrogen dioxide. The of product of the degradation, nitrogen dioxide, is reportedly reactive and attacks the remaining PETN resulting in additional decomposition pathways (Chambers et al., 2002).

Formation of the strong oxidiser easily leads to the oxidation of the alkoxy radical to peroxy radicals (ROO·) (Kimura, 1989). This further explains further release of nitrogen dioxide as detected by IR spectroscopy performed on the gaseous species evolved during isothermal decomposition analysis. These isothermal decomposition studies revealed initial degradation products comprising nitrogen dioxide and formaldehyde (CH₂O) (Makashir and Kurian, 1999). Thereafter followed nitric oxide (NO), nitrous oxide (N₂O), carbon monoxide (CO) and carbon dioxide (Makashir and Kurian, 1999).

Miller et al. (1982) studied the isothermal decomposition of PETN at selected temperatures below the melting point. The study determined the activation energies for the formation of several decomposition products. From the results they suggested the potential for additional decomposition mechanisms as activation energies shift drastically with a decrease in temperature. The production of nitrous oxide and water proceeds along a single mechanism due to similar activation energies while other products are produced by different mechanisms in the a temperature range of 90 °C to 135 °C (Miller et al., 1982).

2.6.2 Chemical incompatibilities and degradation catalysts

Decomposition can further be accelerated by contact with certain additives or impurities in the explosive. A variety of materials have been shown to accelerate the degradation of high explosives, these include molybdenum trioxide (MoO_3), copper (Cu), and nickel (Ni) (Mileham et al., 2008, Kwok et al., 2002, Makashir and Kurian, 1999, Gromov et al., 2009).

The study by Mileham et al. (2008) attempted to find chemical incompatibilities between PETN and metal oxides. In the investigation PETN was deposited on the surfaces of a variety of metal oxide powders which were then stored at a temperature of 50 °C for a period of several months. Analysis was performed over the span of the study to determine the long term degradation effects, if any, due to the contact with the metal oxide. Molybdenum trioxide accelerates the degradation of PETN is (Mileham et al., 2008).

Mileham et al. (2008) reported a difference in DSC results when micron sized molybdenum trioxide was used in place of nano-particles. DSC analysis performed on samples which consisted of nano-molybdenum trioxide coated with PETN showed that the decomposition increased when compared to pure PETN. The difference was thought to be due to the greater surface contact achievable with nano-particles. Kwok et al. (2002) similarly reported a size dependence that lowered the degradation temperatures of RDX in contact with aluminium of various sizes.

2.6.3 PETN initiation

In previous chapters the difficulty of direct replacement of primary explosives with thermites has been discussed. In summary, advances in in thermite processing and compounding have led to compositions with burn rates approaching the velocity of some low order detonations. The problem however remains that that maximum shock pressure still falls below that required for direct initiation (Khasainov et al., 2017).

2.6.3.1 Ignition and combustion

An attempt was made to determine the energy requirements for the ignition of several explosives by Bryan et al. (1958). PETN with a density of approximately 87 % of the TMD was analysed in that study. The authors determined that a heat flux of $1.046 \text{ kJ}\cdot\text{cm}^{-2}$ was required to ignite the PETN sample.

Alternatively, time-to-explosion data can provide information regarding the storage and application stability of an explosive. Henkin and McGill (1952) studied the temperature dependence of decomposition by loading 25 mg PETN samples into enclosed copper tubes. These tubes were then placed into a Wood's metal bath. The bath temperature was lowered for each run until a temperature was reached at which no explosion occurred. The results of the study are summarised in Figure 2-14.

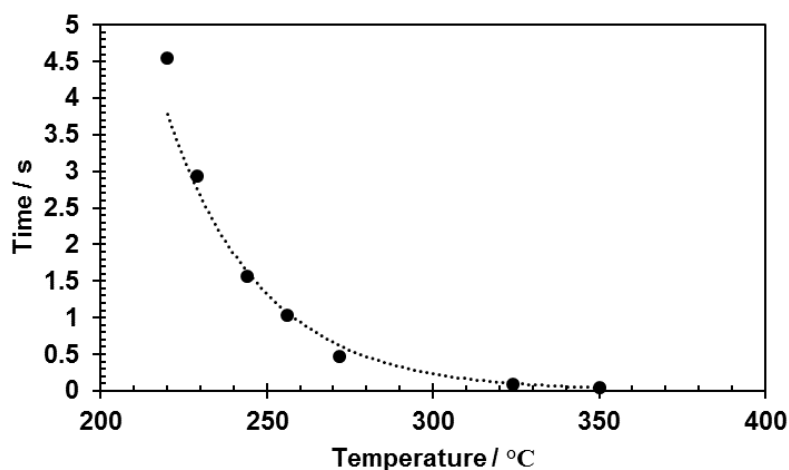


Figure 2-14. Temperature dependence for the onset of thermal runaway in PETN. Adapted from Henkin and McGill (1952).

The data shows a significant temperature dependence with the time to explosion decreasing with an increase in temperature. Henkin and McGill (1952) reported no explosion at a temperature of 215°C or lower. Determining the actual ignition temperature of the explosive is difficult as a variety of factors do affect it such as the heat transfer process from the heat source, pressure, size or mass of reactants, reactant types and reaction rate (Kubota, 2002).

Huang and Wu (1994) estimated the autoignition temperature of high explosives based on single DSC or DTA results. The values estimated for PETN at a heating rate in the range of $6^{\circ}\text{C}\cdot\text{min}^{-1}$ to $15^{\circ}\text{C}\cdot\text{min}^{-1}$ results in temperatures ranging between 158°C and 172°C . The values reported by Huang and Wu (1994) are similar to the calculated auto ignition

temperature of 166 °C determined by Harris (1976). These values are lower than the value reported by Maycock (1970) who from DTA results reported an ignition temperature of 203 °C. Since these estimates depend on peak positions and the slopes of the exotherm differences are expected.

2.6.3.2 Shock initiation

Shock initiation of PETN by means of a projectile is somewhat easier to describe and investigate when compared to the thermally induced DDT alternative. This is mostly due to the abundance of data available for shock initiation. The initial packing density of the explosive is an important factor to consider. Initiation data is usually accompanied by the undisturbed density of the explosive as seen in Figure 2-15 and Table 2.4.

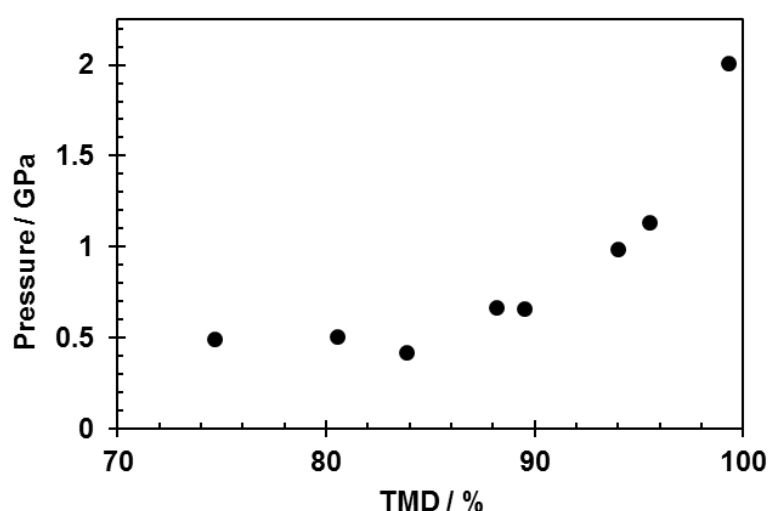


Figure 2-15. Small scale gap test for PETN indicating the critical pressure relation to PETN density. Adapted from (Bauer, 1975).

Table 2-4. Critical energy requirement for PETN initiation

Density ($\text{g}\cdot\text{cm}^{-3}$)	E_c ($\text{J}\cdot\text{cm}^{-2}$)
$\sim 1^1$	8.4
1^1	11.3
1.2^2	1.2
1.4^2	8.6
$\sim 1.6^1$	16.7
1.6^2	14

1 (Cooper, 1996) ,2 (Schwarz, 1975)

The data show that lower density samples of PETN are easier to initiate. Furthermore, the run distance is shorter for lower density samples when exposed to the same shock pressure, see Figure 2-11.

Tanguay and Higgins (2004) mention significant differences in the literature, especially when comparing shock waves passing through a solid interface versus a gas. The critical pressures reported for shock waves delivered from a gas are a full order of magnitude smaller than those reported when a solid was used as the transfer medium (Tanguay and Higgins, 2004). However, shockwaves which produced similar pressure profiles and decay rates resulted in similar critical shock strengths. They concluded that the gas plays no special role in initiation, and that the differences in literature are due to the pressure gradient behind the shock waves.

2.6.3.3 Models

Several authors have modelled the response of PETN in a number of circumstances to various stimuli. These models considered cook-off, decomposition, shock initiation and DDT. Hobbs et al. (2010) modelled the ignition of PETN assuming first order decomposition in all phases. It was also assumed that the reaction rate was independent of pressure and that the activation energy was normally distributed. The model assumed a single-step mechanism with a modified Arrhenius reaction.

Tarver et al. (2003) suggested the thermal decomposition of PETN has four schemes or stages. Each of these stages have different reaction kinetics which is similar to the model of Hobbs. The stages are depicted in Scheme 2-2 to Scheme 2-5

- Scheme 2-2 PETN $\rightarrow$ condensed phase intermediates
- Scheme 2-3 PETN + condensed phase intermediates $\rightarrow$ gaseous intermediates
- Scheme 2-4 Condensed phase intermediates $\rightarrow$ gaseous intermediates
- Scheme 2-5 Gaseous intermediates $\rightarrow$ final gaseous products

As has been mentioned PETN decomposition starts before reaching the melting point, which then necessitates the first stage, Scheme 2-2, to be in the condensed phase. Tarver et al. (2003) assumed the first phase to be solid or liquid bond breaking reaction with the most likely being the O-O₂ bond. Scheme 2-3 and Scheme 2-4 represent the autocatalytic degradation. The final stage represented in Scheme 2-5 is a highly exothermic gas phase reaction leading to the final gaseous products CO₂, H₂O, N₂ and CO (Tarver et al., 2003).

It is clear that the phase the material finds itself in has a big influence on the rate equations. When implementing the decomposition or ignition rate equations in more complex models describing initiation the problem gets significantly more complex. Consider a properly confined column of PETN that has already progressed past the initial stages of DDT. It has been shown

that the process of DDT does change to a degree depending on the particle size of the PETN (Gifford et al., 1999, Gifford et al., 2002). It was remarked that by using very fine PETN particles at low densities the compressive burning stage is avoided, thereby preventing plug formation (Gifford et al., 1999). Recalling the stages of DDT mentioned in Chapter 2.4.2 the formation of a plug is caused by compressive burning. It is this plug which in turn initiates a shockwave as it is driven into the remaining column of unreacted explosives. Without plug formation the process for DDT of fine PETN powder would have to be significantly different. Gifford et al. (1999) showed that the transition of fine PETN behaves according to type II DDT. This is a similar manner of initiation as demonstrated by tetryl and picric acid. Transitions of this kind occur without the formation of shockwave that initiates the unreacted part of the column. Instead the combustion reaction rapidly proceeds along the full length of the column which then leads to a localised thermal explosion (Gifford et al., 1999, Gifford et al., 2002). Ershov et al. (2015) modelled the rapid transition to detonation seen in their previous works when initiation is induced by high temperature gasses. Their model incorporated particle fragmentation as well as erosive and ablative burning effects into account. No individual effect could adequately describe their experimental data. However, a combination of ablation and fragmentation processes provided a plausible explanation for the Rapid DDT reported.

Modelling of these systems is a difficult endeavour due to the complexity of the initiation process. To illustrate this the model of Sáenz and Stewart (2008) will be discussed in more detail. It describes the DDT transition of a porous PETN bed where initiation is caused by impact. The model could also reasonably replicate thermal ignitors with the selection of the appropriate boundary conditions. The model developed by Sáenz and Stewart (2008) can be broken down into the following parts:

1. Euler, reaction and compaction progress equations;
2. EOS for fully dense condensed explosives;
3. EOS for porous explosive;
4. Compaction rate; and
5. Reaction rate.

Euler, reaction and compaction progress equations. As discussed in Chapter 2.3 momentum, mass and energy balances are necessary to solve a shock problem. The problem becomes more complex due to the effect the shockwave has on the bed. At the same time the extent of the reaction will also influence system parameters. To account for this Sáenz and Stewart (2008) uses both a compaction (ϕ) and a reaction progress (λ) variables.

The overarching model in one dimension is shown in Equations 2-92 to 2-95 (Sáenz and Stewart, 2008).

$$\frac{\partial \mathbf{u}}{\partial t} + \frac{\partial \mathbf{f}}{\partial x} = \mathbf{S} \quad 2-92$$

$$\mathbf{u} = \begin{bmatrix} \rho \\ \rho u \\ \rho \left(e + \frac{u^2}{2} \right) \\ \rho \phi \\ \rho \lambda \\ \rho u \end{bmatrix} \quad 2-93$$

$$\mathbf{f} = \begin{bmatrix} \rho u^2 + p \\ \rho u \left(e + \frac{u^2}{2} + \frac{p}{\rho} \right) \\ \rho u \phi \\ \rho u \lambda \end{bmatrix} \quad 2-94$$

$$\mathbf{S} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ \rho r_\phi \\ \rho r_\lambda \end{bmatrix} \quad 2-95$$

The inclusion of compaction variables is a feature in these models since bed density plays an important role (Ershov et al., 2013, Stewart et al., 1994). The compaction variable has a limit of one for a fully compacted bed. Sáenz and Stewart (2008) defined the reaction progress as the ratio of mass products to the total mass of a relative volume element. Solving this set of differential equations requires an EOS as well as definitions for the two rate equations seen in Equation 2-95.

Equation of state (EOS). For the reactants and products Sáenz and Stewart (2008) used the wide-ranging EOS (WR-EOS). A summary of the EOS will be discussed here as used by Sáenz and Stewart (2008) a more in depth discussion of the EOS can be found in (Wescott et al., 2005). The specific internal energy (e) and pressure (p) of the products and reactant are shown in Equations 2-96 to 2-99

$$e_p(p, v) = e_p^s(v) + \frac{v}{\Gamma_p(v)} (p - p_p^s(v)) \quad 2-96$$

$$p_p(e, v) = p_p^s(v) + \frac{\Gamma_p(v)}{v} (e - e_p^s(v)) \quad 2-97$$

$$e_r(p, v) = e_r^s(v) + \frac{v}{\Gamma_r(v)} (p - p_r^s(v)) \quad 2-98$$

$$p_r(e, v) = p_r^s(v) + \frac{r_r(v)}{v} (e - e_r^s(v)) \quad 2-99$$

In the preceding equations the subscript (r) indicates reactants while (p) is used for products. The super script (s) is used to indicate when the function is defined on the isentrope passing through the CJ state (Sáenz and Stewart, 2008). The specific volume is indicated by v . These are just a part of the equations necessary to describe the reactants and products at the various stages of the initiation process. The supporting equations and calibration method can be found in Sáenz and Stewart (2008).

Compaction rate. Bed compaction is an endothermic process that occurs due to shifting grains, pore collapse and grain deformation (Sáenz and Stewart, 2008). In earlier discussions the importance of densification or plug formation was discussed. Sáenz and Stewart (2008) take the change in density into account by relating the compaction rate (r_ϕ) to the pressures experienced by the bed during the initiation event, see Equation 2-100.

$$r_\phi = k_\phi \left\{ p - p_0 - P_h \left[1 - \sqrt{\frac{\phi_0(1-\phi)}{\phi(1-\phi_0)}} \right] \right\} \quad 2-100$$

It is assumed that the compaction rate is proportional the difference between the average pressure in the bed (p) and the equilibrium pressure ($p - p_0$). The parameter (k_ϕ) is related to the dynamic relaxation processes in the bed. The calibration for k_ϕ and the hardening pressure (P_h) is discussed in more detail by Sáenz and Stewart (2008).

Reaction rate equations. As with the decomposition or ignition rate equations discussed earlier, the model transitions between a slow and a fast rate. The rate equation used in the model utilises a switch in order to take the slow and fast reaction forms into account. This is similar to the earlier work done by Xu and Stewart (1997) on DDT in HMX. In that study two distinct regimes for the burn or reaction rate (r_λ) were observed and modelled as such. In the study by Sáenz and Stewart (2008) a similar approach was taken as shown in Equation 2-101 and supporting equations 2-102 to 2-104.

$$r_\lambda = H(p - p_{ign}) k(\phi_0) \left(\frac{p}{p_{cj}} \right)^{\mu(\phi_0)} (1 - \lambda)^{v(\phi_0)} \quad 2-101$$

$$k(\phi_0) = 4.31e^{76.47\phi_0^2 - 142.22\phi_0 + 71.38} \quad 2-102$$

$$\mu(\phi_0) = 25.627\phi_0^2 - 42.504\phi_0 + 20.676 \quad 2-103$$

$$v(\phi_0) = \text{const} = 0.4$$

2-104

In Equation 2-101 a pressure cut off is used ($H(p - p_{ign})$). Sáenz and Stewart (2008) calibrated the reaction rate parameters ($k(\phi_0), \mu(\phi_0), v(\phi_0)$) as shown in Equations 2-102 to 2-104 to fit the distance to breakout data reported by Stirpe et al. (1970).

Solving. The brief summary of the model described so far should indicate that it's a difficult system to solve. Sáenz and Stewart (2008) used a fifth order weighted essentially non-oscillatory (WENO) scheme to for spatial discretisation. A third order Runge-Kutta integration method is used to solve the system of PDEs. A more in depth discussion falls outside of the scope of this work. However Johnsen and Colonius (2006) and (Jiang and Shu, 1996) offers insight into its application, while the review of Zhang et al. (2019) provides further examples of its use and implementation to a variety of systems.

2.7 Fast burning thermites

Thermites, especially nano-thermites, are being investigated as possible alternatives to primary explosives. Direct replacement of primary explosives with pyrotechnic alternatives are prone to failure due to the differences in the reaction rates (Martirosyan et al., 2012, Khasainov et al., 2017). A simple comparison can be made between thermites and high explosives in order to illustrate this. Comparing the reactive power of pyrotechnics with primary explosives will illustrate the difference in energy release rate. The calculation of which can be done with Equation 2-105 (Bockmon et al., 2005).

$$\text{Reactive power} = \Delta H_c u \rho_{bulk} A_{cross} \quad 2-105$$

The reactive power is a function of the average combustion velocity (u). For this reason it will be significantly lower when comparing thermites to high explosives (Bockmon et al., 2005, Jian et al., 2013) The typical detonation velocity of primary explosives is in the range of $3.5 \text{ km} \cdot \text{s}^{-1}$ to $5.5 \text{ km} \cdot \text{s}^{-1}$ (Klapötke, 2012) . This is significantly faster than the linear burn rates produced by thermites, even nanothermites do not achieve burn rates within that range.

To illustrate the performance differences Bockmon et al. (2005) compared the reactive power of aluminium molybdenum trioxide compositions with that of composition B (a mixture of 59.5 % RDX, 39.5 % TNT and 1 % wax). The reported reactive powers for the thermites ranged from 600 kW to over 1000 kW, while that of composition B was $6.72 \times 10^8 \text{ kW}$. This example

illustrates the drastic difference in performance when comparing a fast burning thermite to a detonation.

The reaction rate and therefore the reactive power of thermites are significantly lower than detonating high explosives. This does not mean that they cannot be used to replace primary explosives. It does, however, imply that an alternative initiation method is required. The flying plate detonator Glavier et al. (2017) devised, illustrates this. It employed a pyrotechnic charge ahead of an RDX charge to drive the plate. The particles in the compositions used were in the nanometer range. Due to their fast reaction rates, a significant pressure pulse developed during the burn. Nano-thermites offer significant benefits over their micron scale counterparts with respect to much faster burn rates, and through that more intense pressurisation. Table 2-5 lists a few examples high performance thermites.

Table 2-5. Examples of fast and or gas generating thermites studied by a variety of authors

Composition	ER	Size		TMD (%)	Burn rate (m·s ⁻¹)	Peak pressure (MPa)
		Fuel	Oxidiser			
Al/CuO ^(a)	1.6	80 nm	Nano rods	-	2200	-
Al/CuO ^(b)	1.1	80 nm	21 nm × 100 nm	6	802	13.1
Al/CuO ^(c)	1	80 nm -150 nm	240 nm	30	340	16.7
Al/Bi ₂ O ₃ ^(b)	1.3	80 nm	2 µm	17	646	53.4
Al/Bi ₂ O ₃ ^(c)	1	80 nm -150 nm	100 nm - 500 nm	30	420	21.6
Al/MoO ₃ ^(b)	1.4	80 nm	30 nm × 200 nm	11	950	18.62
Al/MoO ₃ ^(c)	1	80 nm -150 nm	90 nm – 6 µm	30	100	7.4
Al/WO ₃ ^(b)	1.85	80 nm	100 nm ×20 nm	9	952	26.89
Al/PTFE ^(c)	1	80 nm -150 nm	800 nm – 1.5 µm	30	2	21.4
Al/I ₂ O ₅ ^(d)	1	100 nm	10 nm - 100 nm	-	2000	~11

(a) (Apperson et al., 2007), (b) (Sanders et al., 2007), (C) (Glavier et al., 2015), (d) (Martirosyan, 2011, Martirosyan et al., 2009a)

The examples shown in Table 2-5 illustrate the difference components can have on the performance of a thermite, but it also highlights the variability found when using the same components. Pyrotechnic reactions are complex due to the fact that fuels and oxidisers are separate solid entities that may, or may not, undergo phase changes during the reaction (Berger, 2005, Brown, 2001, Wang et al., 1993). This means that the reaction can be solid-solid, solid-liquid, solid-gas etc. The presence of multiple components and phases complicates

matters when trying to identify rate determining properties. In a review on pyrotechnic reactions Berger (2005) identified several parameters that influence a pyrotechnic reaction. The parameters are as follows:

- Type of chemicals;
- Oxygen balance;
- Active surface area;
- Presence of binders or additives, and
- Degree of mixing.

In other words, the choice of fuel and oxidiser combinations will influence the burn rate. The ratios in which they are combined plays an important role in ignitability and propagation. All of this is complicated even more by the addition of binders or other additives. The particle size of the individual components affects the performance of the composition. This is because reactions generally occur with at least one component in the solid phase. With the reaction taking place on the surface of the reactant a larger active surface area will be beneficial.

Since fuels and oxidisers are separate entities the quality of mixing can also drastically influence the performance of a composition. Care should also be taken with selection of the mixing method as certain compositions will not be compatible with some of them. Material selection also affects mixing protocols. For example, while nanomaterials provide better performance, this comes with increased sensitivity which makes mixing large quantities potentially risky. Thus far only the composition has been mentioned, but the environment or device in which the composition is used will also alter its combustion rate (Focke et al., 2018).

2.7.1 Chemical selection

In its simplest form a pyrotechnic composition consists of a solid fuel mixed with a solid oxidiser. The selection of the fuel and oxidiser depends on a number of factors. The most important of which is the intended goal for the composition. Pyrotechnic compositions are used for a variety of applications. They find use as propellants, ignitors, smoke and noise generators to name but a few applications (Conkling and Mocella, 2019). In order to optimise certain performance criteria, or to assist with processing, additives are sometimes included in a composition. Binders may also be used for certain applications.

2.7.2 Fuels

Pyrotechnic fuels can be metallic such as aluminium or non-metallic as in sulfur (S), or organic compounds such as sugar (Conkling and Mocella, 2019). Several fuels will be briefly discussed in this section.

Aluminium is a widely used fuel in all kinds of pyrotechnic systems and devices. It owes its widespread use to its relatively low cost and stability (Conkling and Mocella, 2019). It is also readily available in a variety of shapes and forms, such as flake or spherical particles. Aluminium owes its stability to its protective oxide coating that forms under ambient conditions. This coating prevents the underlying fuel from unwanted oxidation. Due to its widely studied nature, much is known about the oxidation of aluminium in a variety of environments (Dreizin and Schoenitz, 2015, Hasani et al., 2012). It has been shown that there are various stages of aluminium oxidation. These stages are the result of changes in the oxide layer covering unreacted aluminium. In summary the four stages are (Dreizin and Schoenitz, 2015):

- I. Growth of amorphous oxide;
- II. Amorphous transition to $\gamma\text{-Al}_2\text{O}_3$;
- III. Growth of $\gamma\text{-Al}_2\text{O}_3$ with $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ transitions; and
- IV. Growth of $\alpha\text{-Al}_2\text{O}_3$.

During stage I, the aluminium resists oxidation due to the protective nature of the amorphous oxide layer cover. At temperatures approaching 900 K the transition to $\gamma\text{-Al}_2\text{O}_3$ is initiated. The transition leads to an increase in the rate of oxidation (Hasani et al., 2012, Dreizin and Schoenitz, 2015). This is due to the change in density from the amorphous to $\gamma\text{-Al}_2\text{O}_3$. This increase in density results in a significantly thinner oxide layer covering a particle due to the dimensions of the face centred cubic $\gamma\text{-Al}_2\text{O}_3$ crystals (Dreizin and Schoenitz, 2015). Oxidation causes the growth of the $\gamma\text{-Al}_2\text{O}_3$ layer in stage III. This is accompanied by transitions to aluminium oxides with similar densities and face centred cubic structures, e.g. $\gamma\text{-Al}_2\text{O}_3$ (Dreizin and Schoenitz, 2015). At temperatures exceeding 1200 K the transition to $\alpha\text{-Al}_2\text{O}_3$ occurs. The shift to the hexagonal close packed polymorph of alumina results in a significant increase in density (Dreizin and Schoenitz, 2015). Due to the thickness of the oxide layer at this point it will consist of multiple layers of dense crystals. This reduces the diffusivity decreasing the rate of further oxidation.

Magnesium (Mg) is an easily ignitable fuel (Conkling and Mocella, 2019). It has found widespread use in pyrotechnic devices. It does however readily react with moisture which can lead to degrading the performance of composition (Conkling and Mocella, 2019). Magnalium

is an alloy of aluminium and magnesium. The alloy has a lower melting point than either of the constituents at 460 °C (Conkling and Mocella, 2019). It has found use in incendiary devices the same as aluminium and magnesium.

Zirconium is known for producing very hot reactions (Conkling and Mocella, 2019). It is for this reason that it has found some use in ignitors and incendiary devices, where its ignition sensitivity and high reaction rate is beneficial (Fischer and Grubelich, 1996, Yen and Wang, 2012). More widespread use is hampered by its extreme spark sensitivity (Conkling and Mocella, 2019). Its use in nano-thermites has been limited by the difficulty of producing it on the nano-scale (Comet et al., 2019) and its high price (Yen and Wang, 2012) .

Sulfur has long been used in pyrotechnic compositions such as black powder. It is not the most efficient fuel due to a low heat output. For that reason, its inclusion in compositions is usually with the intent to act as a tinder or flux (Conkling and Mocella, 2019). Sulfur has a variety of allotropes which means its chemical and physical properties can vary significantly (Meyer, 1976). It is due to this feature that a variety of melting points are reported in literature which may lead to confusion. β -sulfur has a melting temperature of approximately 119.6 °C (Meyer, 1976). The use of sulfur, and compounds containing it, have been linked to environmental and health issues (Sun et al., 2017, Karim, 2013). Environmentally, sulfur oxides have been linked to the formation of acid rain and some of the health concerns have led to investigations to find suitable replacements (Sun et al., 2017).

Carbon is widely used in pyrotechnics usually in the form of charcoal. It is usually used when a relatively fast burn rate is required in conjunction with a high heat and gas output (Conkling and Mocella, 2019). An example of a well-known charcoal-fuelled system is black powder (Oxley, 2003). Carbon is also used as an additive to assist in ignition or increase a composition's gas generating potential (Conkling and Mocella, 2019, Tursynbek et al., 2020)

Boron (B) has a high melting point which may make it difficult to ignite when paired with certain oxidisers (Conkling and Mocella, 2019, Yen and Wang, 2012, Comet et al., 2019). Boron is relatively expensive but has found use in igniters and as an additive to other compositions where its high heat output on a mass basis can be beneficial (Conkling and Mocella, 2019). Boron has also been investigated as a fuel for pyrotechnic delay compositions and as a fuel additive in other energetic formulations (Focke et al., 2018, Yen and Wang, 2012).

Silicon (Si) is very similar to boron but it is relatively inexpensive. It finds widespread use in time delays and igniters (Conkling and Mocella, 2019, Koch and Clément, 2007, Focke et al.,

2018). A composition consisting of silicon and bismuth trioxide (Bi_2O_3) has been investigated as a sensitizer for the aluminium and copper(II) oxide composition (Ilunga et al., 2011). Silicon has received attention as a possible component in primary explosive-free initiators. Nanoporous silicon reacts explosively when combined with the certain oxidisers. In order to take advantage of the large active surface area, it is usually paired with oxidisers that can be dissolved and recrystallized within the porous structure (Clément et al., 2005, Koch and Clément, 2007).

2.7.3 Oxidisers

There are a wide variety of oxidisers available for use in compositions. Similar to the fuel selection, the purpose and operating conditions should be kept in mind when selecting components. For example, oxidisers that decompose to produce significant volumes of gas may work in propellants while being ineffective when used in an enclosed pyrotechnic delay. Fuel and oxidiser compatibility also plays a role in selection. Table 2-6 lists a couple of commonly used oxidisers.

Table 2-6. Commonly used oxidisers and their melting points

Compound	Formula	Melting point (°C)
Ammonium nitrate	$\text{NH}_4(\text{NO}_3)_2$	170 ^(a)
Potassium nitrate	KNO_3	334 ^(a)
Iron(III) oxide	Fe_2O_3	1565 ^(a)
Copper(II) oxide	CuO	1026, decomposes ^(b)
Red lead	Pb_3O_4	500 ^(a) , decomposes
Potassium periodate	KIO_4	582 ^(a) , decomposes
Potassium perchlorate	KClO_4	610 ^(a)
Bismuth trioxide	Bi_2O_3	279 ^(c)
PTFE	C_2F_4	350 ^(d) , pyrolysis
PCTFE	C_2ClF_3	211-216 ^(d)

(a)(Conkling and Mocella, 2019) (b)(Pourmortazavi et al., 2008, Chadda et al., 1989) (c)(Baijot et al., 2015) (d) (Koch, 2012)

Nitrates such as ammonium nitrate and potassium nitrate are strong oxidisers. Potassium nitrate has a long history of use in pyrotechnic compositions dating as far back as the invention of black powder. Compared to ammonium nitrate, potassium nitrate is less water soluble (Conkling and Mocella, 2019). Both of the oxidisers undergo endothermic decomposition (Agrawal, 2010). Potassium nitrate is known to produce fast reactions when paired with the appropriate high-energy fuel (Conkling and Mocella, 2019). Care should be taken when using ammonium nitrate as it can undergo detonations under the certain conditions (Conkling and Mocella, 2019). Ammonium nitrate is a relatively inexpensive oxidiser that is used in situations where high levels of gas generation are required (Agrawal, 2010).

Iron(III) oxide and its combination with aluminium produces the well-known “thermite” reaction. Due to its high melting point, systems utilising this oxidiser are known for their high ignition temperatures (Conkling and Mocella, 2019). When paired with the correct fuel it produces a significant amount of slag in an essentially gasless reaction (Conkling and Mocella, 2019). Iron oxide also finds use as an additive in composite propellants. It is added as a catalyst to these systems enhancing the burn rate of the propellant (Agrawal, 2010). An interesting development is the ability to make energetic aero- or xerogels using iron(III) oxide as the oxidiser (Teipel, 2005). These composite mixtures allow for intimate fuel-oxidiser contact within a porous structure (Teipel, 2005).

Red lead is used in gasless delay compositions (Agrawal, 2010, Focke et al., 2018). It was also used in the crackle formulations in fireworks (Conkling and Mocella, 2019). Due to environmental concerns it is being phased out (Tichapondwa et al., 2015, Conkling and Mocella, 2019).

Sulfates have been investigated for a variety of applications. Calcium sulfate has been investigated as a possible replacement for heavy metal based oxidisers in pyrotechnic delays (Tichapondwa et al., 2015). Copper sulfate (CuSO_4) is a possible component in a composition to replace lead-based primary explosives (Yi et al., 2018). Persulfates have also been investigated as potential biocidal compounds (Zhou et al., 2015).

Copper(II) oxide and bismuth trioxide are both oxidisers that have received a lot of interest when fast burn rates or rapid gas production is required. These two oxidisers were extensively studied for use in nano-energetic gas generators (Glavier et al., 2017, Glavier et al., 2015, Baijot et al., 2015, Fleck et al., 2017, Shaw et al., 2013, Patel et al., 2015, Puszynski et al., 2007, Staley et al., 2014, Staley et al., 2013, Apperson et al., 2007, Martirosyan et al., 2012, Martirosyan, 2011, Martirosyan et al., 2009a, Martirosyan et al., 2009b, Piekel et al., 2014, Wang et al., 2011). When paired with a good fuel such as aluminium, these two oxides produce fast burn rates and high pressure pulses. See Table 2-5. Depending on the thermite in question, the process of gas generation will differ. The high pressures reported for the bismuth trioxide systems are thought to be due to the relatively low boiling point of bismuth metal. The combustion temperature of bismuth trioxide and composition is approximately double that of the vaporisation temperature of bismuth or its oxide which are 1564 °C and 1344 °C respectively (Baijot et al., 2015). Copper(II) oxide is believed to undergo a rapid initial decomposition releasing oxygen which is responsible for the pressure rise witnessed within its systems. In either case, the gas formation is crucial for accelerating the reaction due to improved heat transfer routes available (Egan et al., 2016). Bismuth trioxide has also found

use in delay compositions. Interestingly in this application, when paired with silicon, it burns in an essentially gasless manner (Focke et al., 2018).

Iodine-based oxidisers such as potassium periodate and sodium periodate (NaIO_4) have received a lot of interest of late as potential replacements for perchlorates (Conkling and Mocella, 2019, Brusnahan et al., 2017). Iodine-based oxidisers also find use in devices designed to defeat hazardous biological agents (Clark and Pantoya, 2010, Wang et al., 2015). Unlike potassium perchlorate, the decomposition of the potassium and sodium periodate is endothermic (Conkling and Mocella, 2019). Periodate-based compositions have received interest as nano-energetic gas generators as well as for potential green alternatives to primary explosives (Wan et al., 2019, Zhou et al., 2017, Jian et al., 2013).

Fluorine is a powerful oxidiser, in reality it is the most energetic oxidiser (Agrawal, 2010). It is for this reason that fluorine containing compounds have found widespread use in pyrotechnic applications, acting as energetic binders, oxidisers or in surface passivation (Valluri et al., 2019). Table 2-6 shows two examples of fluorine-containing polymers used in pyrotechnics. Polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE) are both very good oxidisers. PTFE contains four fluorine atoms in its monomer while PCTFE has three and an additional chlorine atom which itself is also a good oxidiser. MTV consists of magnesium, Teflon and Viton. It is a well-known pyrotechnic composition used for decoy flares (Koch, 2012). Teflon and Viton are du Pont trade names for the PTFE and vinylidene fluoride-hexafluoropropene copolymer (VDF-HFP) respectively. In this example the PTFE is the oxidiser while the Viton acts as an energetic binder.

Fluorine is such a powerful oxidiser that it will in fact react with aluminium oxide to produce aluminium fluoride (AlF_3) (Osborne and Pantoya, 2007, Mulamba and Pantoya, 2014, Sippel et al., 2013, Kim et al., 2017). Aluminium used in combination with a fluorine containing oxidiser, e.g. polytetrafluoroethylene, can undergo exothermic pre-ignition reactions (Aravind et al.). Mulamba and Pantoya (2014) found that pre-ignition reactions are influenced by the chain length of the PTFE. The reactions produce an Al-F layer on the particle surface. The aluminium core is therefore separated from the surroundings by an aluminium oxide layer with a thin outer layer consisting of aluminium fluoride. This reinforced external coating effectively seals off the core. It allows the aluminium to melt completely causing an increase in the core pressure, thereby enhancing the melt dispersal mechanism (MDM) (Mulamba and Pantoya, 2014).

2.7.4 Additives and binders

Additives are used to modify the burn rate, assist with processing, prolong shelf life, modify sensitivity while in some cases colourants are used (Berger, 2005, Focke et al., 2018, Khan et al., 2018, Tichapondwa et al., 2016). Ignition aids or sensitizers are used to assist with the ignition of a composition to a particular stimulus. Sulfur, present in certain compositions, ignites at a lower temperature than the bulk composition itself. In the process it initiates the combustion of the rest of the composition. Inert abrasives are also used to increase the friction sensitivity of some compositions. Compounds, such as copper(II) oxide, decrease the ignition temperature by catalysing the decomposition of the other components including oxidisers (Focke et al., 2018).

Binders are used to improve cohesion between fuel and oxidiser particles (Agrawal, 2010, Khan et al., 2018). Natural and man-made binders are used to protect the composition from moisture and improve mechanical strength of the composition (Agrawal, 2010, Focke et al., 2018). Care should be taken when selecting the binder and formulating the loading level as they have the capacity to drastically alter the combustion performance of the composition (Focke et al., 2018, Khan et al., 2018). Fluorinated binders such polyvinylidene fluoride (PVDF) improve ignition performance of aluminium based systems as discussed earlier in the chapter. On the other hand, binders can also have detrimental effects by reducing thermal conductivity or removing heat from the system by means of volatilisation (Focke et al., 2018, Khan et al., 2018).

Inclusion of these compounds may lead to different phases being present, changes in thermal conductivity and oxygen balance which in turn may either improve or decrease the reaction rates (Focke et al., 2018, Tichapondwa et al., 2016). It may also play a role in determining the compounding techniques that can be used. These factors should be considered when including extra components into the base composition.

2.7.5 Composition

Depending on the intended goal certain compositions will immediately be ruled out whereas others can find use in multiple applications or devices. Not only should the pyrotechnic composition be able to work within its intended device, but it should also comply with the following criteria (Conkling and Mocella, 2019):

- Cost efficient;
- Simplicity of manufacture;
- Safety during manufacture, transport and use;

- Sensitivity should fall within the allowed range for intended purpose;
- Stability during storage, and
- Reasonably low environmental impact.

What makes a fuel more or less suited for an application? Referring back to the Chapter 2.2 and in particular Equation 2-1 the Gibbs free energy of formation of the oxides can be used to compare possible fuels. An Ellingham diagram is used as preliminary tool for comparing potential fuels over a temperature range (Focke et al., 2018). An example of such a diagram is shown in Figure 2-16.

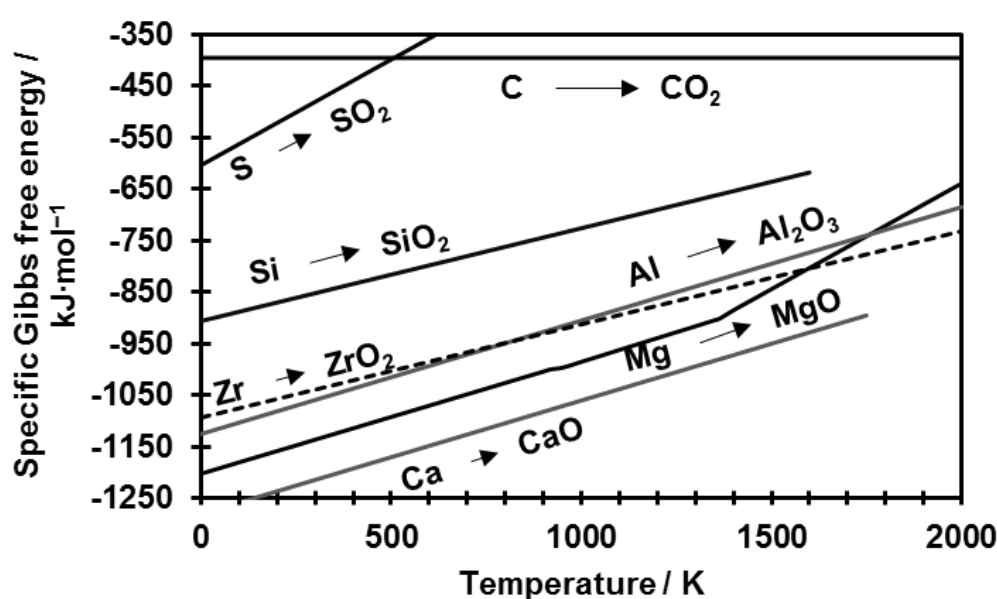


Figure 2-16. Ellingham diagram for potential fuels adapted from DoITPoMS (2021), oxygen provided at partial pressure of 101.325 kPa.

Possible fuel and oxidiser combinations can be determined by comparing their relative positions on the graph. A fuel should occupy a lower position on the graph than the potential oxidiser (Focke et al., 2018). When comparing the Gibbs free energy of formation for aluminium, magnesium, calcium and silicon, it is clear that at lower temperatures calcium and magnesium have more negative values of the Gibbs free energy. Aluminium, however, shows better performance at higher temperatures since calcium and magnesium experience a rapid drop in reducing potential (Wang et al., 1993). Furthermore, calcium as with other alkaline earth and alkali metals, excluding magnesium, are too reactive with moisture and atmospheric oxygen to be viable fuels (Conkling and Mocella, 2019). This makes storage and processing difficult if not hazardous.

The choice of chemicals extends beyond just that of selecting a fuel. When trying to select an oxidiser, it is helpful to look at its heat of decomposition and its melting point. The heat of decomposition is an indication of the oxidiser stability. A high heat of decomposition will require a fuel that releases a lot of energy during its oxidation in order for the reaction to be self-sustaining (Conkling and Mocella, 2019). Wang et al. (1993) suggests comparing the exothermicity of systems when trying to identify valid compositions. This requires calculating the theoretical heat of reaction and maximum adiabatic temperature as discussed in Chapter 2.2.1. The theoretical maximum temperature of the system provides insight into the phases partaking in the reaction (Wang et al., 1993). If the heat released by the reaction is sufficiently high that it can raise the temperature of the adjacent composition to its ignition temperature the composition will burn in a self-sustained manner. A good starting point for binary compositions is a survey by Fischer and Grubelich (1996) which provides an extensive list of fuel and oxidiser combinations as well as calculated adiabatic reaction temperatures and heats of reaction. The calculated adiabatic temperatures listed are an important indicator when trying to determine if a reaction will self-propagate. A temperature in excess of 2000 K is considered the requirement for self-propagating combustion (Wang et al., 1993).

The melting point of the oxidiser provides an indication of the temperature where oxygen will start to be liberated (Conkling and Mocella, 2019, Moghaddam and Rees, 2003). At this point a reaction can commence should the fuel be in a receptive state. Ignition sensitivity ties into phase change temperatures and the nature of oxide degradation. Phase change and decomposition temperatures should be considered when designing a composition as the reactivity of the composition will increase when one or more of the constituent components undergo a phase change (Moghaddam and Rees, 2003, Yen and Wang, 2012). This is due to the improved contact that can be obtained between the reactants when one or more of them are not in the solid phase. Fuels like silicon and boron which have high melting points and can be difficult to ignite when paired with certain oxidisers due to the lack of phase transitions (Conkling and Mocella, 2019). It is also known that fuels with low melting points, such as sulfur and other organic fuels, generally have lower ignition temperatures than metal-fuelled compositions (Agrawal, 2010).

Thermal analysis of the individual components is a useful method to try and determine how a fuel and oxidiser will interact. However, the melting and decomposition temperatures of the neat components may not provide a complete picture as can be inferred from Table 2-7.

Table 2-7. Thermal analysis results of pyrotechnic systems

Component	Temperature (°C)		
	Melting	Decomposition	Ignition
Al ^(a)	660		
Mg ^{(a)(b)}	650		
S ^(b)	119		
KMnO ₄ ^{(a),(c)}	-	240 ^(a) -284 ^(c)	
CuO ^(a)		1026	
KNO ₃ ^{(b)(d)}	334	547 ^(d)	
KClO ₃ ^(b)	356	400	
Ba(NO ₃) ₂ ^(c)	592	690	
NH ₄ ClO ₄ ^(c)	-	310	
Compositions			
Al/CuO ^(a)	248.7	-	289.7
Al/Ba(NO ₃) ₂ ^(c)	-	-	624.9
Mg/KMnO ₄ ^{(a),(c)}	292 ^(a)	-	306.2 ^(a) -302.9 ^(c)
Mg/CuO ^(a)	382	-	431
Mg/KNO ₃ ^(b)	-	-	565
Mg/KClO ₃ ^(b)	-	-	540
Mg/NH ₄ ClO ₄ ^(c)	-	-	346.4
S/KNO ₃ ^(b)	-	-	340
S/KClO ₃ ^(b)	-	-	150

(a) (Pourmortazavi et al., 2008), (b) (Agrawal, 2010), (c) (Babar and Malik, 2015), (d) (Yano, 1989)

The phase change in the oxidiser is generally considered responsible for triggering ignition (Moghaddam and Rees, 2003, Oxley et al., 2015). In Table 2-7, the systems containing sulfur ignite at temperatures lower than those of melting and decomposition of the oxidisers it was paired with. Similarly, the systems containing copper(II) oxide feature ignition temperatures lower than the melting or decomposition temperatures of the oxide.

It should be noted however that in these instances ignition occurs before a phase change should occur in the fuel. This is unlike the sulfur-based systems in which it melts before the reaction commences. Some compositions feature melting points lower than that of their constituent components, e.g. in eutectic systems. As with ignition temperature, the mixture's apparent melting point depends on the heating rate.

The nature of oxidiser decomposition should also be considered. Oxidisers that undergo exothermic decomposition can significantly increase the sensitivity of a system, whereas endothermic compositions tend to have the opposite effect (Agrawal, 2010, Conkling and Mocella, 2019). An example of this can be seen when comparing the systems containing potassium nitrate and potassium chlorate (KClO_3). Potassium nitrate has an endothermic decomposition process as opposed to the exothermic decomposition of the chlorate (Yano, 1989, Agrawal, 2010). It is for this reason that it has a higher ignition temperature in compositions compared to potassium chlorate (Agrawal, 2010).

It should be clear by now that the selection of a fuel and oxidiser for a system is a complex process. This process is complicated even further when taking processing considerations and other properties like the particle size of the individual components are considered. Particle size drastically alters the way in which a component reacts. When working with nanomaterials material properties like melting point can be drastically lower than expected.

2.7.6 Fuel to oxidiser ratio

The optimal fuel loading depends on the intended use of the thermite. In the present case it is that of a fast burning gas generator. The calculation of the equivalence ratio was discussed in Chapter 2.2.2. It was also mentioned that slightly fuel-rich systems tend to have higher burn rates. A reason for the faster combustion rates of slightly fuel-rich systems is the higher thermal conductivity of the metallic fuels compared to the solid oxidisers or the surrounding air. Compositions that are slightly fuel rich will therefore have enhanced thermal transport properties which enhances flame propagation (Pantoya and Granier, 2005). Alternatively, the faster burn rates experienced by slightly fuel-rich systems may be due to the reaction of the fuel with atmospheric oxygen (Yen and Wang, 2012). This can be checked by conducting tests under an inert atmosphere. Non-metallic fuels such as silicon or boron also display improved burn rates at higher fuel loadings. For non-metallic fuels the optimal loading is however closer to stoichiometry due to the lower thermal conductivity (Focke et al., 2018).

2.7.7 Particle size and packing density

2.7.7.1 Particle size

A common theme in Table 2-5 is the use of reactants that are in, or are approaching the nanometer size-range. Micron-sized thermites are usually slow burning and difficult to ignite (Dreizin and Schoenitz, 2015, Levitas et al., 2006, Tichapondwa et al., 2016). Ilunga et al. (2011) reported no change in the ignition temperature for an aluminium-copper(II) oxide

composition when moving from micron- to nano-sized particles. However, the same study reported a 100 °C decrease in the ignition temperature when the particle sizes of the silicon and bismuth trioxide were reduced. This indicates that there is more to improving ignitability than a simple reduction in particle size.

Decreasing the particle size of a component increases the surface area-to-volume ratio. This increases the fraction of the constituent atoms present on the surfaces of the particles (Martirosyan et al., 2012, Kwok et al., 2002). Particles in the nanometer range can have ten percent or more surface atoms (Pantoya and Granier, 2005). Material properties can vary greatly due to this. At particle sizes below 10 nm these changes are drastic (Yetter et al., 2009). Eckert et al. (1993) reported a difference in melting temperature of up to 100 K for milled aluminium nanoparticles between 13 nm and 25 nm. The suggested explanation for this was boundary-induced disorder. This was caused by the distortion of the atomic planes next to grain boundaries in the aluminium and the interface with the aluminium oxide. The decreased ignition temperature of nano-thermites can be attributed to the significant lowering of the melting temperature (Dreizin and Schoenitz, 2015, Kwok et al., 2002, Wang et al., 2011).

Beyond a certain point, further reduction in particle size does not translate into faster burn rates (Sullivan et al., 2014, Yetter et al., 2009). This is attributed, in part, to the decrease in the active fuel content. Most fuels are covered in a native oxide layer. This oxide layer protects the underlying fuel from further oxidation at ambient conditions and even affects its reactivity at higher temperatures (Kwok et al., 2002). In aluminium, this layer is typically 4 nm to 8 nm thick (Pantoya and Granier, 2005). The volume fraction of alumina on an individual particle increases as particle size decreases because the surface oxide thickness remains approximately constant. Figure 2-17 illustrates the reduction in the active fuel content as the particle size decreases.

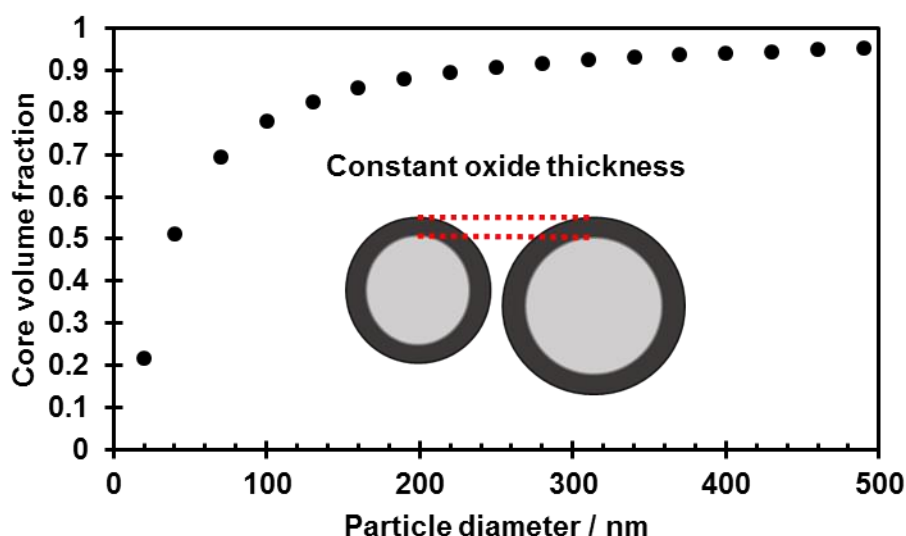


Figure 2-17. Aluminium core volume fraction as a function of particle size.

The reduced fuel content must be accounted for when preparing compositions. The effect it has on the system is more difficult to counteract. The alumina layer has a lower thermal conductivity than that of the aluminium. This can lead to a reduction in the combustion velocity due to the reduced rate of energy transport (Pantoya and Granier, 2005).

Sullivan et al. (2014) investigated the effect of fuel size for an aluminium and copper oxide(II) composition. They varied the aluminium particle size from 108 μm to 80 nm while keeping the oxidiser in the nano-meter size-range. The experimental setup indicated that the reaction followed two distinct regimes depending on the size of the aluminium fuel. The change between regimes occurred at a particle size of 3.5 μm . Sullivan et al. (2014) reported that above 3.5 μm , the burn rate scaled with fuel particle size. However, it was independent of particle size below this value. They reasoned that the flow velocity of the gas reached a maximum that was limited by the pressure gradient, porosity and gas viscosity. Another potential reason is related to the reaction kinetics not scaling with reduction in the particle size.

The effect particle size has on the burn rate of thermites cannot be discussed without mentioning the melt dispersal mechanism (MDM). Models exist which describe aluminium combustion as a diffusion process whereby oxygen passes through the oxide shell to react with the underlying fuel. These models do not however describe burn rates in excess of 1 $\text{km}\cdot\text{s}^{-1}$, which are too fast to be limited by diffusion through aluminium oxide shell (Levitas et al., 2014). Levitas et al. (2006) suggested that the oxide shell remains intact while the aluminium within it heats up. The melting of the aluminium causes internal particle pressures to increase up to 0.1 GPa – 4 GPa. This increase in the internal pressure causes catastrophic

spallation of the oxide shell. The subsequent unloading wave disperses the liquid aluminium (Levitas et al., 2006). This accelerates oxidation since aluminium droplets or clusters are not protected by an oxide layer through which the oxygen has to migrate in order to react with the fuel (Levitas et al., 2014).

The ignition method and applied heating rate influence the ignitibility and reaction rate of a thermite. An example of this is the study by Pantoya and Granier (2005) in which the aluminium molybdenum trioxide system was initiated with a carbon dioxide laser. In this setup, higher combustion velocities were found for micron-sized compositions. The reported faster burn rates are in contradiction to theoretical expectations. DSC analysis and temperature measurements made during the combustion experiments showed that the ignition mechanisms differed. This meant that the combustion velocities could not be directly compared. The nanocomposite ignited at temperatures significantly lower than that of the micron-sized composite. The micron-sized composite only ignited after a significant amount of preheating occurred. The aluminium melted before ignition occurred and sublimation of molybdenum commenced before ignition. The faster combustion velocities were attributed to this liquid-gas reaction mechanism (Pantoya and Granier, 2005). It has been shown that MDM is a factor in the combustion of larger particles (Levitas et al., 2014, Levitas et al., 2008). Heating rates sufficient to stimulate MDM, provide an explanation for the elevated reaction rates observed for the micron-sized composites. Oxidiser size has not been mentioned yet and should also be considered. Table 2-8 contains burn rates for two thermites with varying fuel and oxidiser particle sizes.

Table 2-8 Effect of fuel and oxidiser size on linear burn rate (Weismiller et al., 2011)

Components	Component sizes		Linear burn rate (m·s ⁻¹)
	Al	Oxide	
Al/CuO	Nano	Nano	980
	Micron	Nano	660
	Nano	Micron	200
	Micron	Micron	180
Al/MoO ₃	Nano	Nano	680
	Micron	Nano	360
	Nano	Micron	150
	Micron	Micron	47

The fastest burn rates were reported for systems that have the fuel and oxidiser in the nanometer range. Where only one component was in the nanometer range, the systems containing nano-oxidisers had the fastest burn rates. The explanation for this cannot wholly be described by the dilution effect of the alumina layer mentioned earlier (Weismiller et al., 2011). The increased rates witnessed for nano-oxidisers were attributed to earlier vaporisation of the particles. The reduced particle dimensions also decreased the time needed for the gas to diffuse away from the particle. Weismiller et al. (2011) attributed the higher pressurisation rates reported to be due to these factors. This enhanced the convective burning mechanisms.

The homogeneity of a composition can be improved if the components are in the nanometer range (Pantoya and Granier, 2005, Martirosyan et al., 2012). The improved mixing, increased specific surface area and improved contact between components lead to faster reaction rates. This is due to the decrease in mass transport limitations (Wang et al., 2011, Pantoya and Granier, 2005, Sullivan et al., 2014).

2.7.7.2 Packing density

As with the detonation velocity of high explosives, the burn rate of pyrotechnic compositions is affected by the packing density of the composition. The packing density influences the combustion performance but also depends on the formulation and the particle sizes. Certain formulations will favour a particular combustion mechanism. High densities would not have beneficial outcomes for systems with a convective burning mechanism (Weismiller et al., 2011). The opposite will be true for systems that are dominated by a conductive heat transfer mechanism such as gasless or near gasless systems (Khan et al., 2018).

Referring back to Table 2-5, the highest burn rates are reported for thermites with lower densities. It should be noted however that the listed compositions were all in the nanometer range. In this particle size range, convective combustion mechanisms dominate (Weismiller et al., 2011). The products from thermites comprising aluminium and molybdenum trioxide are expected to remain in the condensed phase. However, Bockmon et al. (2005) suggested that a significant amount of material actually does transition to a gaseous state, causing a pressure gradient to develop. Relatively high pressures, for thermites, were observed during these reactions. This supports a convective combustion mechanism being responsible for the increased rates reported for nano-thermite reactions.

Peak pressure measurements are also affected by packing density (Bockmon et al., 2005, Apperson et al., 2007, Sanders et al., 2007, Glavier et al., 2015). Pressure generally increases with increase in packing density. This depends however, on the system and the mechanism of its reaction. Sanders et al. (2007) demonstrated this by comparing the burn rates and peak pressures in an aluminium-bismuth trioxide system with those for an aluminium-molybdenum trioxide system at a low (<20 %TMD) and high (47 %TMD) density. The density effect varied with composition as shown in Table 2-9.

Table 2-9. Effect of density on combustion performance, adapted from Sanders et al. (2007)

TMD (%) Composition	20		47	
	Burn velocity (m·s ⁻¹)	Pressure (MPa)	Burn velocity (m·s ⁻¹)	Pressure (MPa)
Al/Bi ₂ O ₃	646	53.4	560	39.3
Al/MoO ₃	950	18.6	580	45.5

The results illustrate the difficulty of describing thermite behaviour. The burn velocity decreased in both instances but the pressure output increased for the molybdenum trioxide. Compositions will react differently under compaction and this should be considered when designing a system.

The increase in pressure witnessed for the higher density by the molybdenum trioxide system is an interesting result. According to Bockmon et al. (2005), the increased mass of thermite, confined within the same volume, is a possible explanation for the increased pressure readings at higher densities. This extra mass produced more gas which led to higher pressures. However, this does not explain the reduced performance certain systems experience at higher compaction. This is partially explained by the realisation that the combustion mechanism for most, if not all, nano-thermites is convective in nature. This means that at the high densities (47 % TMD) reported by Sanders et al. (2007) the flow of gaseous components is severely hampered. This explains the reduced combustion velocities but not the large increase in the peak pressure for the one system.

Glavier et al. (2015) reported on a variety of nano-energetic gas generators. He attempted to explain the mechanism of the aluminium molybdenum trioxide reaction by looking at the boiling points of the components involved. Very little or no gas formation was expected for the system in question. That was due to the very high evaporation temperature of molybdenum. This suggested that the reaction yields mostly condensed products. This allows compression to higher densities as convection plays a reduced role in the progression of the flame front. When the reactions occur at the nanoscale, even molybdenum trioxide undergoes phase changes.

Bockmon et al. (2005) estimated that up to 24 % of the mass would be in the gas phase by the time the adiabatic combustion temperature is reached. This is still lower than some of the other systems discussed and may be the reason for the lower compaction sensitivity compared to other systems.

2.7.8 Processing

2.7.8.1 Modifications

In Section 2.7.2, the effect that an oxide layer has on the performance of a fuel was briefly mentioned. Research has shown that for fuels like aluminium and silicon this oxide layer can be removed. Removal of the oxide layer makes the fuel more reactive. This increased reactivity does, however, mean that the fuel will be more susceptible to oxidation by atmospheric oxygen. In order to prevent premature oxidation, methods have been developed to passivate the fuel with other substances altering the surface chemistry to suit the intended goal. It has been shown that removal of the oxide layer and subsequent passivation of the aluminium surface with a variety of substances leads to atmospheric stability as well as increased reaction rates (Mulamba and Pantoya, 2014, Kwon et al., 2007). These substances include:

- Organic acids;
- Hydrocarbons;
- Nitrocellulose, and
- Fluorinated compounds.

Kwon et al. (2007) passivated aluminium nano-powders, produced by the electrical explosion of wires, with a variety of the abovementioned compounds. Samples coated with stearic acid, oleic acid or nitrocellulose featured lower aluminium contents than those passivated by air or a fluoropolymer. The lower aluminium content was an indication of the more permeable nature of these coatings when compared to the polymer or native oxide produced by the passivation in air. Furthermore, It was noted the acids used reacted with the aluminium lowering the aluminium content even before stability could be tested.

Kim et al. (2017) demonstrated the effect of the removal of the alumina layer and subsequent replacement with PVDF has on the energetic behaviour of micron sized aluminium particles. The benefits of this coating included improved thermal stability in an oxygen atmosphere, higher enthalpy of combustion and greater pressurisation rates. In this study, a comparison was made with the same aluminium that had not gone through the oxide removal process, instead it was just mixed with the PVDF. In this case it was reported to have a detrimental

effect on both the pressurisation rate as well as the burn rate. This was thought to be due to the dilution effect of the alumina layer paired with the lower thermal conductivity of the polymer and the alumina (Kim et al., 2017).

Aluminium is not the only fuel that has been modified for pyrotechnic applications. Porous silicon is produced by electrochemical etching of wafers (Koch and Clément, 2007). In the case of silicon powders, the process is based on stain etching (Sailor, 2012). In both processes hydrofluoric acid is used to produce a porous surface finish on the silicon. The processes also remove the protective silicon oxide (SiO_2) layer on the surface. The multi-stage process results in a surface passivated by hydrogen (Sailor, 2012). Further surface stabilization is possible through annealing (Clément et al., 2005). It has been demonstrated that this layer provides resistance against atmospheric oxidation. Explosive results can be achieved by pairing with an oxidiser that can take advantage of the large specific surface area of the porous silicon (Koch and Clément, 2007, Clément et al., 2005). These are just two examples of methods that can enhance the performance of a fuel. Other methods such as milling and grinding are also used to change fuel properties (Focke et al., 2018).

2.7.8.2 Compounding

A variety of methods have been developed to mix pyrotechnic compositions. A homogeneous mixture is crucial for reproducible performance. Some of the more commonly used methods are (Focke et al., 2018, Teipel, 2005, Koch, 2012):

- Precipitation;
- Sol-gel;
- Brush screening;
- Vibrating screens;
- Sonication;
- Slurry mixing followed by spray drying, and
- Extrusion.

The methods listed are used on both an industrial and a lab scale. The selection of a mixing or processing method will depend on the composition, particle size and the intended application in question. For example, precipitation-based mixing can be used when the oxidizer or binder is soluble. This will however not be an effective method of mixing when a composition is required that is not granular in nature. Extrusion may be a better solution if the composition allows for it as in the case of certain propellants and flare compositions.

The mixing or compounding method can also alter the performance of the composition. This stems from the quality of component distribution or contact that can be achieved. Table 2-10 illustrates this by comparing two different mixing methods used for an aluminium sodium periodate (NaIO_4) system.

Table 2-10. Performance comparison between mixing methods for a nano-aluminium sodium periodate based thermite adapted from Wan et al. (2019)

Mixing type	Maximum pressure (MPa)	Average pressurization rate ($\text{GPa}\cdot\text{s}^{-1}$)
Sonication	3.55	1.91
Spray drying	5.66	2.94

The large differences in the results presented in Table 2-10 can determine whether a composition works or fails in an intended role. In this case, spray drying the composition resulted in the encapsulation of the fuel by the oxidiser. This improved the combustion rate as indicated by the pressurisation rate. The increase in the maximum pressure is most likely due to an increase in the extent of reaction, i.e. a more complete reaction occurred for the spray dried composition.

2.8 Fast burning thermites as initiators

The push to replace heavy metal based primary explosives such as lead azide has been mentioned. It has not been discussed how thermites or pyrotechnic devices can be used to assist with or achieve this goal. The following examples of compositions and systems will illustrate a general trend in the research. This is that the pyrotechnic is used as an ignitor that initiates a DDT event in the secondary explosive. Alternatively, devices have been designed that utilise gas generators in a “gun-like” design to produce a shock wave in the target explosive.

Multiple designs and patents exist for primary-free detonators utilising pyrotechnic charges to initiate DDT of an adjacent high explosive within the detonator shell (Wuensche et al., 2012, Dumenko, 2001, Ilunga and Muller, 2011, Jean-Luc Arpin et al., 1999, Cooper, 1999). In most of these designs the detonator shell is reinforced or the pyrotechnic charge along with the DDT region are contained within a reinforced structure. The reason for the reinforcement stems from the time required for the transition to take place as has been discussed earlier. The patent of Jean-Luc Arpin et al. (1999) describes the use of a high-energy pyrotechnic which initiates the base charge in a manner similar to that of a primary explosive. The

composition used potassium perchlorate which has associated health and environmental concerns attached to its use. That said, the results would indicate that a rapid form of DDT occurs as some reinforcement is still required, indicating that the system is close to the efficiency of lead azide. This example and the others referenced indicate the difficulty of finding a substitute for lead azide that can be directly implemented. For this reason, research has been ongoing.

Glavier et al. (2017) studied the use of a composite system consisting of nano-thermites and RDX to propel a flyer into a secondary charge. The device used the nano-thermite to ignite an enclosed RDX charge. The combustion gasses pressurise the chamber up to a point when the flyer shears free and accelerates down a barrel into a receiving charge (Glavier et al., 2017). In this study of the two thermites, aluminium was the fuel while the oxidisers were either copper(II) oxide or bismuth trioxide. Bismuth trioxide proved to be the better oxide for the application. The ignition delay for the RDX was shorter and higher peak pressures developed (Glavier et al., 2017). An earlier study on a variety of nano-thermites showed that faster reaction rates and higher peak pressures were obtained with bismuth trioxide as the oxidiser (Glavier et al., 2015). In the composite system, these properties are beneficial as a higher initial pressure at the time of ignition of the RDX increases the initial combustion rate as per Equation 2-11. Fleck et al. (2017) investigated ability of the same two thermites to destroy a silicon substrate. The bismuth trioxide thermite produced higher thrust values than a copper(II)oxide thermite. Therefore, bismuth trioxide may be a better choice than copper(II) oxide for applications where a high thrust is more important than the burn rate.

Comet et al. (2015) investigated a composite system that for initiating a PETN pellet without requiring the use of a projectile. The energetic composite transitions to a detonation which, in turn, initiates an adjacent PETN pellet. Aluminium was the fuel with either tungsten(VI) oxide (WO_3) or bismuth(III) sulfate ($\text{Bi}_2(\text{SO}_4)_3$) as oxidisers. The RDX content of composites produced by Comet et al. (2015) was 60 wt.%. At this RDX load either thermite did initiate the PETN charge. The density of the tungsten(VI) oxide-based nanocomposite ranged from 27 % to 29 % of the TMD while the bismuth(III) sulfate system the density ranged from 27 % to 30.5 % of the TMD (Comet et al., 2015). Similarly Martin et al. (2018) reported a detonatable composite containing aluminium, tungsten(VI) oxide and RDX. According to Martin et al. (2018), the low density at which this “new” class of energetic material works effectively represents a limitation. These systems only detonate at a sufficiently low density. Any settling, and thereby densification, of the powder is therefore a problem from a handling and storage perspective.

Yi et al. (2018) reported direct initiation of the secondary explosive RDX by a sulfate-based nano-thermite. However, this direct method of initiation has more in common with standard DDT than the above-mentioned designs. The experimental setup relied on two layers of RDX of varying density. The layer in direct contact with the thermite had a low density and provided the shock necessary to initiate the adjacent high density RDX pellet. The thermite in this instance acted as an igniter of the first section of RDX. The thermite used, consisted of aluminium as fuel and copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) as the oxidiser. The thermite also contained 5 wt.% nitrocellulose as binder (Yi et al., 2018). The use of the sulfate as the oxidisers has several benefits compared to copper(II) oxide. The sulfate oxidizer generated higher peak pressures in addition to significantly higher pressurisation rates (Yi et al., 2018).

A similar system has been demonstrated with sodium periodate (NaIO_4) as the oxidiser. The system could directly cause a deflagration to detonation transition when placed in a loosely packed form adjacent to a PETN column (Wan et al., 2019). The use of sodium periodate is interesting as this type of compound has been considered as an oxidiser for “green” flash compositions. Flash compositions are widely used in fireworks, stun grenades, training devices and simulation devices (Krone and Treumann, 1990, Klapötke et al., 2013, Hahma, 1996). These compositions are usually based on aluminium mixed with potassium perchlorate (KClO_4) and potassium nitrate (KNO_3) (Klapötke et al., 2013, Krone and Treumann, 1990, Moretti et al., 2012). These compositions are considered dangerous due to their easily ignitable nature (Klapötke et al., 2013, Krone and Treumann, 1990). As mentioned, periodates are potential alternatives to the harmful perchlorates (Moretti et al., 2012, Brusnahan et al., 2017, Poret et al., 2013, Jian et al., 2013).

Recently periodate-based systems have attracted interest as replacements for primary explosives (Wan et al., 2019). The authors highlighted the enhanced performance obtainable by intimate contact between fuel and oxidiser. Thermites, in which the nano-aluminium is coated by sodium periodate, were obtained by spray drying the mixtures. The encapsulated aluminium composition was able to initiate a detonation event in a column containing PETN followed by RDX (Wan et al., 2019). The same composition, just mixed by sonication, was unable to initiate steady detonation within the PETN column (Wan et al., 2019).

The systems discussed, all used nano-thermites while, in some of them, a micron sized composition could possibly achieve the same effect provided some adjustments are made. A possibility could be systems in which the thermite acts as a gas generating igniter. Direct

substitution in more complex systems such as the “gun-style” initiator may be more difficult. This is due to the drastic performance differences.

2.9 Analysis techniques

2.9.1 Differential thermal analysis (DTA)

The DTA is used to determine phase change temperatures and the ignition onset temperatures for reactions. The technique subjects a sample and a standard to a controlled heating program. The temperature difference between a sample and a standard is measured and reported as a function of temperature (Skoog et al., 2007).

2.9.2 Bomb calorimetry

Constant volume calorimetry is used to determine the heat of combustion of fuels (Kotz et al., 2010). The sample is placed in a thick-walled steel vessel. This vessel is pressurised using oxygen or an inert gas if the sample contains its own oxidiser. The vessel is submerged in a well-insulated water filled vessel (Kotz et al., 2010). The bomb and surrounding water is heated by the combustion of the sample. The temperature change of the water is measured. This can in turn be used to calculate the change in internal energy for the system, which includes the water and the bomb. The heat released by the reaction is responsible for this change in internal energy since the volume remains constant (Kotz et al., 2010).

2.9.3 Scanning electron microscopy (SEM)

Scanning electron microscope techniques allow for higher resolution images to be captured compared to traditional microscopy (Skoog et al., 2007). The instrument consist of the following (Mohammed and Abdullah, 2018, Skoog et al., 2007) :

- Electron gun;
- A column or path for electrons;
- Scan coils;
- Sample chamber; and
- Display.

The electron gun provides the electrons, usually at an energy of 1 keV to 30 keV (Skoog et al., 2007). The beam provided by the electron source is condensed to a smaller focal point by the magnetic condenser and objective lenses (Skoog et al., 2007). The focal point has a diameter of 2 nm to 10 nm (Mohammed and Abdullah, 2018, Skoog et al., 2007). Scanning of the sample is accomplished through the scan coils. The two pairs of electromagnetic coils are

located in the objective lens (Skoog et al., 2007). Scanning is controlled by providing an electrical signal to a pair which directs the beam impact.

The electron beam interacts with the solid it is imparted on. The interactions of the solid target can be classified as elastic or inelastic (Skoog et al., 2007). Elastic interactions affect the trajectories of the electrons in the beam without a significantly impacting their energy (Skoog et al., 2007). During inelastic interactions part of or all of the energy from the electrons are imparted to the solid after which the exited solid releases secondary electrons (Skoog et al., 2007). The electron detector is used to detect backscattered and secondary electrons from the sample (Mohammed and Abdullah, 2018). The image is then constructed and displayed on the viewing screen.

2.9.4 X-ray diffraction (XRD) and X-ray fluorescence (XRF)

XRD analysis provides a means for qualitative analysis of crystalline powder (Skoog et al., 2007). Each crystalline material has a unique X-ray diffraction pattern which can be used for qualitative identification (Skoog et al., 2007). When the sample, e.g. a crystal surface, a fraction of that beam will be scattered. The remainder of the beam will penetrate into the second layer of atoms and more of it scatters. The process continues as the beam penetrates into the deeper layers of the material. The scatter is caused by the electric vector of the radiation that interacts with the electrons in the atoms of the material (Skoog et al., 2007). Interference occurring between the scattered rays can be constructive or destructive. X-ray diffraction requires that the spacing between atomic layers be roughly the same as the wavelength of radiation (λ). Furthermore, The scattering centres should be spaced in a highly regular way (Skoog et al., 2007). Samples are ground to a fine powder. This allows for a large amount of variation in crystallite orientation fulfilling Bragg's condition for reflection from every possible interplanar spacing (d). The condition for constructive beam interference is shown in Equation 2-106 (Skoog et al., 2007).

$$\sin \theta = \frac{n\lambda}{2d} \quad 2-106$$

If the angle (θ) at which incident X-rays the does not satisfy condition destructive interference occurs (Skoog et al., 2007). In 2-106 the diffraction order (n) is an integer. The powdered sample is placed in a sample holder and mounted in the instrument. The diffraction pattern is recorded. The obtained diffraction pattern is then compared to a database in order to identify the components.

Elemental analysis is achieved through XRF analysis. Sample elements are excited using a beam from an X-ray tube or a radioactive source (Skoog et al., 2007). The samples then emit their own characteristic fluorescence X-rays. The X-Rays generated in this manner are not only from the surface of the sample but also from atoms in deeper within (Skoog et al., 2007). This means that both the incident and the fluorescent radiation have a significant amount of sample to travel through (Skoog et al., 2007). In this time absorption or scattering can take place. For quantitative measurements the relative line intensity reaching the detector is important. The line intensity will be affected by the concentration of the element in the sample bulk as well as matrix effects such as absorption (Skoog et al., 2007). Methods have been developed in order to compensate for matrix effects. One such method is dilution with a material that only weakly absorbs X-rays, e.g. boric acid.

2.9.5 Particle size distribution and surface area

Particle size analysis is performed using dynamic light scattering (DLS) the sample is well-dispersed in a medium. Standard equipment consists of (Skoog et al., 2007):

- A laser source and lens;
- Sample cell;
- Apertures;
- Photomultiplier tube;
- Amplifier and discriminator; and
- Computer with correlator.

The dispersed sample is illuminated by a single-wavelength laser (Skoog et al., 2007). the photodetector measures scattered light from the sample usually at an angle of 90° from the incident beam (Skoog et al., 2007). The detector output is can be processed utilising photon-counting techniques (Skoog et al., 2007). Particle size information is then determined from the a correlation analysis performed on the processed signal.

3 Experimental

3.1 Materials and characterisation

3.1.1 Materials selection

The aluminium used in the study was supplied by Grinman South Africa. Sigma-Aldrich was the source of the copper(II) oxide, potassium periodate and sulfur. The PTFE powder used was sourced from Alfa Aesar. A proprietary sealing and starter composition, G, was provided by AEL Mining Services along with the electric fuse heads. The PETN used in the detonator trials was used as received from AEL.

3.1.2 Characterisation techniques and methods

3.1.2.1 Particle size

A Malvern Mastersizer Hydrosizer 2000 was employed to measure the particle size of individual components. It uses dynamic light scattering to determine the particle size distribution. Water was the dispersant for all the pyrotechnic materials used. Ultrasound and vigorous stirring was employed throughout the tests to break down agglomeration. Samples were run 10 times and averaged results are reported. Particle size analysis could not be performed on potassium periodate and potassium iodide (KI) since they are water soluble.

3.1.2.2 Surface area

The specific surface area was analysed using Brunauer-Emmett-Teller (BET) theory. This was done using a Micrometrics Tristarr II machine. Nitrogen was used as the probing gas for all samples. Samples were degassed at a temperature of 100 °C for a period of 8 h. Degassing took place in the Micrometrics VacPrep 061 Sample Degas System. The software used to perform the analysis was, Tristar II 3020. Samples were run in sets of three.

3.1.2.3 X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was done using a Bruker D8 Advance diffractometer with a 2.2 kW (Cu K α radiation $\lambda=1.5406$ nm) fitted with a LynxEye detector with a 3.7° active area. Scans were done in reflection mode in the angular range 5° to 90° 2 θ .

3.1.2.4 X-ray fluorescence (XRF)

The aluminium was prepared as boric acid briquettes while the sulfur was prepared as a pressed powder. The analysis was performed on ARL'X Sequential XRF instrument. Uniquant

software was used to for this analysis. The software has a detection range between sodium (Na) and uranium (U). Elements within this range are reported when detected.

3.1.2.5 Microscopy

A scanning electron microscope (SEM) was used in order to study the morphology of the unmixed compounds. The microscope used for this analysis was a ZEISS Gemini ULTRA Plus field emission SEM at 1.00 KV. Samples were prepared using a SEM auto-coating unit E2500 (Polaron Equipment Ltd.) sputter coater to deposit a thin carbon layer on the sample surface.

3.2 Mixing

3.2.1 Oxidiser combinations

The compositions stoichiometrically were mixed according to the following reaction schemes:



The resulting binary compositions had aluminium mass contents of 18 %, 24 % and 26.5 %. The aluminium mixture with potassium periodate is the composition that served as the base while the other compositions used as additives. Mixing of the aluminium and potassium periodate was done with either screen brushing or by solvent based methods. In the first case the potassium periodate used was first ground down using a coffee grinder and brushed through a 25 µm sieve before use.

The aluminium powder was brushed through a 25 µm screen before use. A dilute solution of potassium periodate was produced by dissolving the material in boiling water. Potassium periodate has a relatively low solubility at room temperature. Boiling water was used to reduce the volume of water required to dissolve the powder. Aluminium was added to the potassium periodate solution and thoroughly dispersed with magnetic stirring. This mixture was slowly added to ethanol whilst stirring vigorously. Centrifugation was used to separate the powder from the water ethanol mixture. This was followed by oven drying at 70 °C overnight. The recovered powder was then brushed through a 45 µm screen in order to break down agglomerates. Dry mixing was done by brushing the powders through a 25 µm screen. This process was repeated four times for each composition. Compositions containing the recrystallized potassium periodate and or PTFE were mixed using a 45 µm screen according to the procedure described.

3.2.2 Fuel combinations

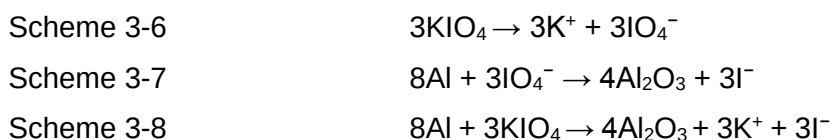
Sulfur was added to the base (Al/KIO₄) system in the form of one of two compositions. These compositions are shown in Scheme 3-4 and Scheme 3-5.



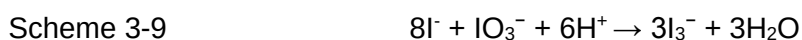
The two compositions have a sulfur mass content of 64.0 % and 21.8 % respectively. The pre-screened aluminium and sulfur composition was prepared following the dry mixing procedure outlined above using a 45 µm screen. For the potassium periodate and sulfur composition the potassium periodate was recrystallized in a similar manner to that described in Section 3.2.1 and then mixed with the sulfur by brushing the components through a 45 µm screen. This process was also repeated four times.

3.2.3 Iodine test

Iodine in solution would indicate that a reaction occurred between the aluminium and the dissolved potassium periodate. A possible route for the reaction is shown in Scheme 3-6 to Scheme 3-8.



The manifestation of the above reaction can be proved by means of a starch iodine test. The blue starch iodide complex that forms during this test is the result of the reaction between starch and the triiodide (I₃⁻) ion (Lambert, 1951). The formation of which is shown in Scheme 3-9 (Lambert, 1951).



The reaction schemes aim to demonstrate that the reagent that causes a colour change in the presence of starch can be produced should a reaction occur between aluminium and the potassium periodate solution. This implies that the addition of starch to the coating process can be used as a simple test to determine if there is a liquid phase reaction taking place during mixing. Should a colour change occur within the coating solution then it can be assumed that a portion of the periodate ions have reacted with the aluminium releasing free iodide ions

which can in a manner similar to Scheme 3-9 form triiodide which is capable of interacting with the starch.

A water soluble starch, dextrin ((C₆H₁₀O₅)_n) was chosen for this test. A solution was produced by dissolving 3.3 g of dextrin in 75 ml of distilled water. The potassium periodate solution was prepared in the manner described in Chapter 3.2.1. After the aluminium was added to the solution three samples were taken from the solution. Each sample was approximately 15 ml. 4 ml of the dextrin solution was added to two of the samples the other one was kept unaltered to serve as the control. Approximately 50 mg of potassium iodide was added to one of the samples containing the dextrin solution. The process was repeated over the course of 15 minutes with samples being taken every 5 minutes.

3.3 Thermal analysis

Differential thermal analysis (DTA) was done on a Shimadzu DTA-50 Differential Thermal Analyser. Samples analysed had masses ranging from 10 to 15 mg. The analysis was done in an argon (Ar) atmosphere provided at a flow rate of 100 ml·min⁻¹. The samples were heated in alumina crucibles from ambient conditions to a maximum of 1000 °C at a rate of 50 °C·min⁻¹. The reference sample was γ-Al₂O₃ provided by Shimadzu.

3.4 Sensitivity analysis

Impact, friction and electrostatic sensitivity were measured for all compositions that were used in subsequent detonator trials. At this point the tests were only done in such a manner to allow for the use of the compositions at the testing facility and should be considered preliminary. A simple go, no-go method was employed in order to gain a basic understanding of the sensitivity to these kinds of stimuli.

A BAM Fall Hammer BFH-10 was used to determine the impact sensitivity of the compositions. The drop weight had a 5 kg mass and all tests started at 1 m in height as the samples were expected to be relatively insensitive to this kind of initiation. The drop height was lowered as necessary until a pass rate of fifty percent was achieved at a given height.

The friction sensitivity of the materials was tested on a BAM Friction sensitivity tester FSKM. Tests were conducted until five consecutive passes were achieved at a level. Electrostatic sensitivity was tested using the OZM ESD 2008A electrostatic spark tester. Samples were subjected to sparks of decreasing energy until ten no-go results were achieved for a specific output.

3.5 Combustion Performance

3.5.1 Burn rates

Open burns were conducted to determine the viability of the composition. If it would not ignite in the presence of atmospheric oxygen, the likelihood of the composition burning in a less ideal environment is unlikely. For open burns the compositions were loosely packed in a groove machined into a pyrophyllite block. The square groove was 4 mm wide 2 mm deep and 150 mm long. At the ignition end G composition was placed. Ignition was facilitated by exposing the G composition to the flame of a butane torch. A Canon powershot SX260 SH camera was used to record the burn rates.

In order to measure enclosed burn rates, the pyrotechnic compositions were loosely filled into silica tubes. The tubes had an outer diameter of 6.1 mm with a wall thickness of 1 mm. The composition spanned a length of 120 mm. G composition was loaded onto the composition to ensure ignition. For systems containing potassium periodate, a layer of approximately 60 mg of the copper oxide thermite was added between the G composition layer and the sample. This was required in order to ensure reliable ignition. The silica tubes were further confined within a steel housing. Samples were ignited using an electric fusehead fixed to the tube by a second steel sleeve.

The burns were monitored through three viewports machined into the steel housing. The total measurement distance was 116 mm. The burns were monitored using an IDT NX8-S2 camera. The frame rate was adjusted as needed for the different samples. The experimental layout and composition housings are shown in Figure 3-1.

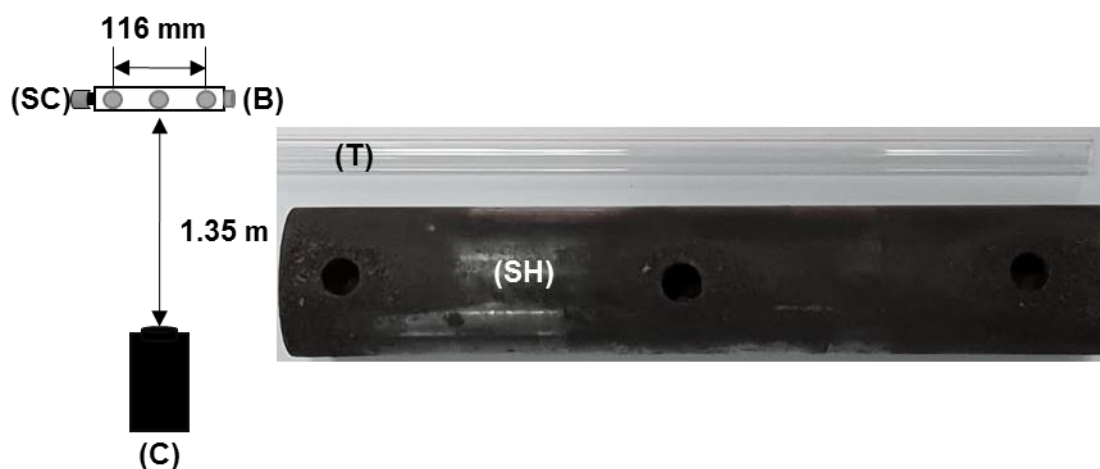


Figure 3-1. Illustration of the experimental setup as well as an example of the silica tube and steel housing used. The camera is indicated by (C), steel collar (SC), bolt (B), steel housing (SH) and silica tube (T).

The steel collar was used to fit the fusehead to the silica tube. Since the silica tubes were open-ended, a plug was used to prevent the composition from being ejected at the end after ignition. Also the force imparted by the fusehead was sufficient to move the tube position within the housing. To remedy both abovementioned problems, the one end of the steel housing was threaded. A bolt was turned into this end fixing the position of the silica tube between it and the steel collar. It also prevented the composition from being ejected during a run.

3.5.2 Calorimetry

A Parr 6200 calorimeter utilising an 1104B 240 mL bomb was used for these trials. The bomb was pressurised to 3000 kPa with helium. The G starter composition (250 mg to 300 mg) was ignited with a nichrome wire. The G composition was added to initiate the main composition. To determine the heat of reaction of the G composition sample sizes of 2.5 g - 2.8 g were required. The other compositions required smaller sample sizes. Sample sizes varied between approximately 550 mg and 1000 mg for the various repeats for each composition.

Each run was adjusted for both the nichrome wire heat output and the heat of reaction of the G composition mass used to facilitate ignition. After which the heat of the reaction could be determined.

3.5.3 Pressure measurements

Combustion pressure was determined utilising the same 1104B 240 mL bomb used for calorimetry. A different head was used which held the Kistler 211B1 piezoelectric pressure transducer. Sample sizes ranged from 500 mg to 600 mg for the composition. G composition was used to assist with ignition and was loaded to a mass of 200 mg. Compositions were run at atmospheric pressure in air or at 3 MPa in helium. Ignition of the system was facilitated by a nichrome wire. Data was recorded at 100 kHz using TCE V3.24 software.

3.5.4 Temperature measurements

A similar setup to that used for the open burns was used to determine the combustion temperature. Approximately 500 mg of each sample was placed on a pyrophyllite block. The samples were lightly compacted into a 25 mm long and 10 mm wide layer. G composition was used as the starter composition and ignition was facilitated using a butane torch. The pyrometer was a Raytek model RAYMM1HVF1L positioned at a distance of 0.5 m from the sample. The software used for analysing the pyrometer signal was DataTemp® multidrop

3.6 Detonator tests

The compositions were tested in live chemical delay detonators. The powder was loaded into the delay element which was placed directly onto an approximately 800 mg charge of PETN. The basic layout of the detonator test assembly is shown in Figure 3-2.

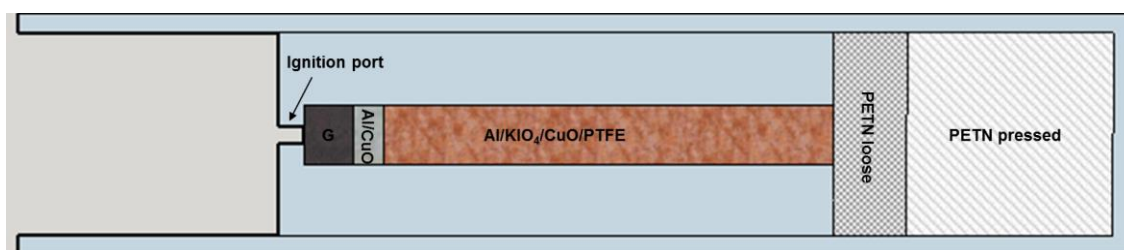


Figure 3-2. Detonator assembly.

3.6.1 Preliminary detonator assembly and testing

The intent of initial trials was to discover if there were any unforeseen problems that would arise once the compositions were loaded into a detonator. It was suspected that the low densities required may make assembly using current automated process problematic. The method used for filling delay elements consists of incrementally loading elements pressing each layer to a pre-set height or density to achieve a consistent burn rate. Transport and handling of detonators can shift the density profile within a detonator that has not been pressed sufficiently.

Loaded elements were then inserted into the detonator shell containing the PETN charge as depicted in Figure 3-2. For the purposes of the tests, two layers of PETN were used with the first not being compacted. This was done in order to improve ignitability. The bulk of the PETN was pressed to a higher density in order to increase the output should the PETN detonate. Shock tubes and electric fuse heads were used in order to initiate the detonators in these trials.

3.6.2 Initial tests with the base system

For these tests an aluminium detonator shell was used. 25 mm aluminium delay elements were used to contain the composition. Depending on the tests, the delay housings already contained pressed G composition in either one or two increments (50 mg per increment). G composition provided a sealing of the tube in addition to igniting the subsequent layer of Al/CuO composition. The G composition was consolidated by loading the press to 1176 N. The Al/CuO composition was added on top of the pressed layer of G. Followed by the Al/KIO₄

based system. These two compositions were not pressed but were allowed to settle “naturally” by vigorously tapping the element. Layer thickness was determined by recording X-ray images of the elements. The masses of the individual compositions were varied in this stage of testing to identify potential problems.

The aluminium shells used initially were replaced by copper shells as tests proceeded. This was done in order to allow for better confinement, providing an improved chance for a deflagration to detonation transition.

3.6.3 Improved loading procedure and modifications

Later on, the increment masses were decreased. This allowed better compaction thereby increasing the composition loading and leading to enhanced ignition consistency. Beyond increasing the number of increments the press was also used to consolidate certain increments. The first increment consisted of G composition and it ranged in mass between 50 mg to 60 mg. This increment was then pressed using 540 N of force. The next increment was also G composition with a mass ranging between 30 mg to 45 mg. This the increment was pressed again using half of the force used for the first layer. The third increment consisted of the Al/CuO composition. Approximately 40 mg to 60 mg of this composition was tap filled onto the previous two layers. This was followed by five increments of the Al/KIO₄/CuO/PTFE composition. Each of these ranged between 60 mg to 80 mg. After the fifth layer, the column was pressed using 245 N of force. A sixth layer of composition, approximately 100 mg, was added to the column and pressed at 100 N. This revised loading procedure drastically reduced the number of column misfires.

The detonator shell and loading procedure was also altered in these trials. A change was made to copper shells and later to a copper-nickel alloy in an attempt to prevent bursting and retain confinement. The base charge was kept at approximately 800 mg of PETN. The base charge was loaded in two increments the first 700 mg was loaded then pressed using 1176 N. The second increment was 100 mg and remained un-pressed to allow for facile ignition.

3.7 FPD detonator design and testing

It was mentioned in Chapter 2.5 slapper and flying plate detonators function by accelerating a projectile into the secondary explosive. The impact of this projectile generates the shock wave that induces detonation of the secondary explosive. The basic mechanism is similar in function to a rifle in that a projectile is accelerated down a barrel by the combustion of a propellant charge.

Where direct shock initiation or DDT through a thermal ignition method may not be viable for the chosen composition, a “gun style” initiator may provide a solution.

3.7.1 Ballistic measurements

The factors that affect the projectile velocity and initiation potential have been discussed. A simple gun style detonator was designed to test the potential of the composition. The design was based on the aluminium delay elements used up to this point. This was done to keep it as close to the detonator design used earlier in this Chapter. Mild steel was used for the element instead of aluminium.

Elements had an outer diameter of 6.2 mm with an internal diameter of 3.95 mm. Two element lengths were used 27 mm and 29 mm. Projectiles were ball bearings with a diameter of 3.96 mm and mass of 260 mg. This meant that the bearing was slightly larger than the barrel allowing it to be held in place without crimping the tube. This was done in an attempt to simplify the design. In the design the projectile is forced down the “barrel” using a press. Friction and the minor deformation caused by this action is what keeps the projectile within the element.

Figure 3-3

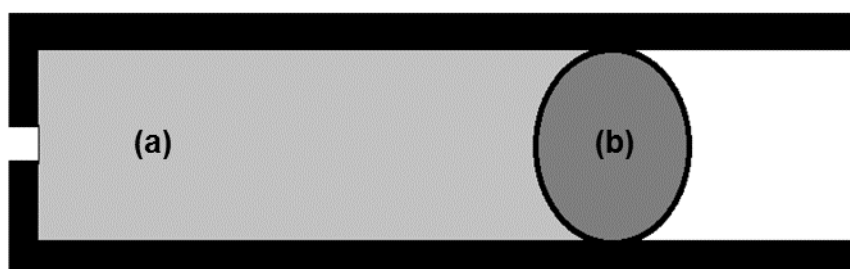


Figure 3-3. FPD (a) combustion chamber, (b) projectile.

The composition loading procedure was similar the improved loading procedure discussed earlier. Individual increment masses where adjusted slightly. The G composition was loaded in two increments of approximately 60 mg and 30 mg. This was followed by a 60 mg increment of the Al/CuO composition. The Al/KIO₄/CuO/PTFE composition was then loaded in 5 increments of approximately 75 mg followed by a final increment of approximately 115 mg. A press was used to consolidate the compositions. This was done after the first and second increments of the G composition and the fifth and sixth increments of the Al/KIO₄/CuO/PTFE.

3.7.1.1 Projectile velocity

For these tests a brass housing unit was used to hold both the element and electric fuse head. The unit was closed and held in a vice with the help of a 2 mm thick steel plate. The plate had a 5 mm diameter hole to provide sufficient space for the projectile to leave the assembly, while stopping the element from leaving. An example of the assembly without the steel stopping plate is illustrated in Figure 3-4.



Figure 3-4. The open element housing containing an element and fuse head.

Projectile velocity was determined by reviewing the footage of the event recorded with the high-speed camera. The same camera was used to film the event as was used for the enclosed burn rate trials, see Chapter 3.5.1. The measured velocity, together with the other projectile properties, were used to calculate the magnitude of the shock that could be imparted on a target material. The experimental setup for the velocity tracking of the projectile is shown in Figure 3-5.

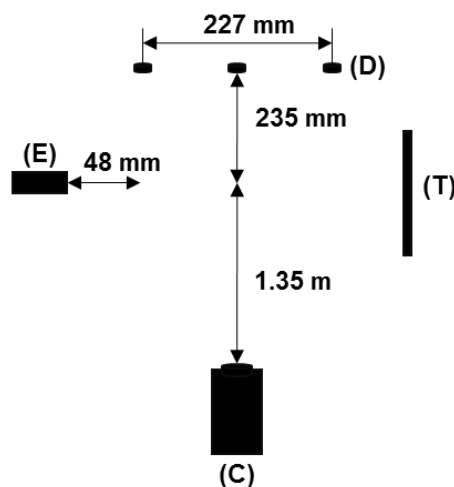


Figure 3-5. Experimental setup for projectile velocity measurement. The element is indicated by (E), the camera by (C) and the target (T). Three rows of calibration dots are indicated by (D).

The exposure time varied between 13 μs and 15 μs with a frame rate of 12000 or 12500 fps. The region of interest had a width of 1568 pixels and a height of either 375 pixels or 368 pixels, the latter for the higher frame rate. Pixel depth was set to 10 bit.

The muzzle velocities for the elements were determined by comparing the velocity vs. distance data, to predictions from the ballistic formulas for spherical projectiles reported by Allen (2018). In these equations, the atmospheric temperature was set to 15 °C while the relative humidity and atmospheric pressure were set at 40 % and 101.325 kPa. The actual data was overlaid on predictions for muzzle velocities ranging from 300 $\text{m}\cdot\text{s}^{-1}$ to 700 $\text{m}\cdot\text{s}^{-1}$ in order to find the best fit for the data.

3.7.1.2 Impact illustration

Aluminium witness blocks were used as targets to quantify the magnitude of the impact that the projectiles delivered on a target. The blocks had a mass of 340 g to 354 g and were 28 mm thick. The blocks were placed 0 cm, 5 cm and 24 cm away from the element. For all placements the blocks were not securely fixed in place. This was done allow pressure release for the target placed at 0 cm, and to prevent or at least reduce ricocheting. Initiation of the elements occurred in the manner described earlier.

For comparison purposes an aluminium block was dented on a press using the same ball bearings used as projectiles. This data was used to estimate the magnitudes of the forces that produced the indentations found on firing of the projectiles. The dimensions used for the force and work calculations are shown in Figure 3-6.

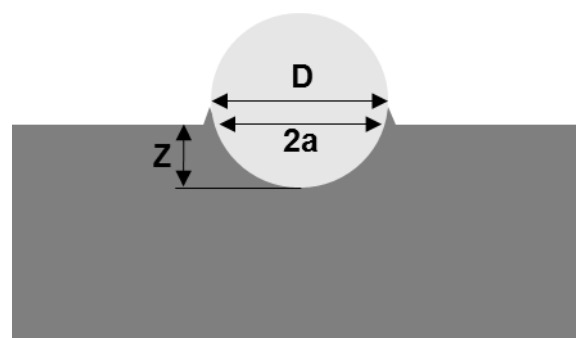


Figure 3-6. Crater dimensions, depth (z) and radius (a), caused by a rigid penetrator of diameter (D), adapted from (Byrnside and Torvik, 1971).

The rigid penetrator theory for projectile penetration is used. The theory considers the projectile to be a rigid Brinell indenter and allows for penetration up to one projectile diameter

(Byrnside and Torvik, 1971). Geometry is used to determine the depth of penetration from Equation 3-1

$$2Z = D - \sqrt{D^2 - 4a^2} \quad 3-1$$

The link between the applied force and the size of the indentation is described by Equation 3-2 (Byrnside and Torvik, 1971).

$$F = k(2a)^n \quad 3-2$$

The material constants (k and n) in this equation were determined from the data acquired by the manual pressing of the witness blocks. With these values known, the energy transferred (i.e. work done) by the impact force of the impacting projectile was determined using the work energy theorem, shown in Equation 3-3.

$$w = \int F dx \quad 3-3$$

Equation 3-5 is found through substituting 3-2 into 3-3 (Byrnside and Torvik, 1971).

$$w = k \int_{z_0}^{z_f} (2a)^n dz \quad 3-4$$

In Equation 3-5 Work done on the target is calculated from the point where there is no deformation or cratering (Z_0) up to final depth of the crater (Z_f). In its current form the crater is at its final radius (a). the expansion of the crater can be accounted for by using Equation 3-1 (Byrnside and Torvik, 1971), see Equation 3-5.

$$w = k \int_0^d \frac{(2a)^{n+1}}{\sqrt{D^2 - 4a^2}} da \quad 3-5$$

Equation 3-5 takes the change in crater radius (a) into account. It ranges from 0 to the final crater radius of (d). Integration yields the work required to produce the crater. It should be remembered that this relationship is limited to penetrations up to but not exceeding one projectile diameter.

3.7.2 Detonator testing

For live detonator testing, the PETN loading in the detonator shell was altered. This was necessary to prevent the PETN from occupying space within the barrel of the initiating element that was placed on top of it. In the altered procedure, the loose layer of PETN was omitted and only a base charge of approximately 700 mg PETN was directly pressed into the detonator shell. Ignition was achieved by means of a shock tube.

4 Results

4.1 Particle size and surface area

Table 4-1 reports the particle size distribution as well as the BET surface areas for the materials used.

Table 4-1. Particle size distribution and BET surface area for the components used

Compound	D ₁₀ (µm)	D ₅₀ (µm)	D ₉₀ (µm)	BET surface area (m ² ·g ⁻¹)
Al	6.0	13.2	29.1	0.17 ± 0.03
CuO	4.4	9.9	18.4	2.39 ± 0.1
Al ₂ O ₃	3.2	11	27.7	54.2 ± 1.79
PTFE	5.3	102	830	1.73 ± 0.12
S ^a	13	29	60	≈1.45
PETN ^b	169	249	369	≈0.03

Values determined by (a) Govender (2018) and (b) supplied by AEL Mining services.

The measured particle sizes of the copper(II) oxide and the PTFE differed significantly from the values indicated by the suppliers. The copper(II) oxide was specified as less than 3 µm while those for the PTFE were supposed to fall within a 6 µm to 10 µm range. Incomplete breakup of agglomerates is a probable explanation. This possibility was explored using electron microscopy.

4.2 Microscopy

SEM imaging results for the major components used in the tests are shown in Figure 4-1.

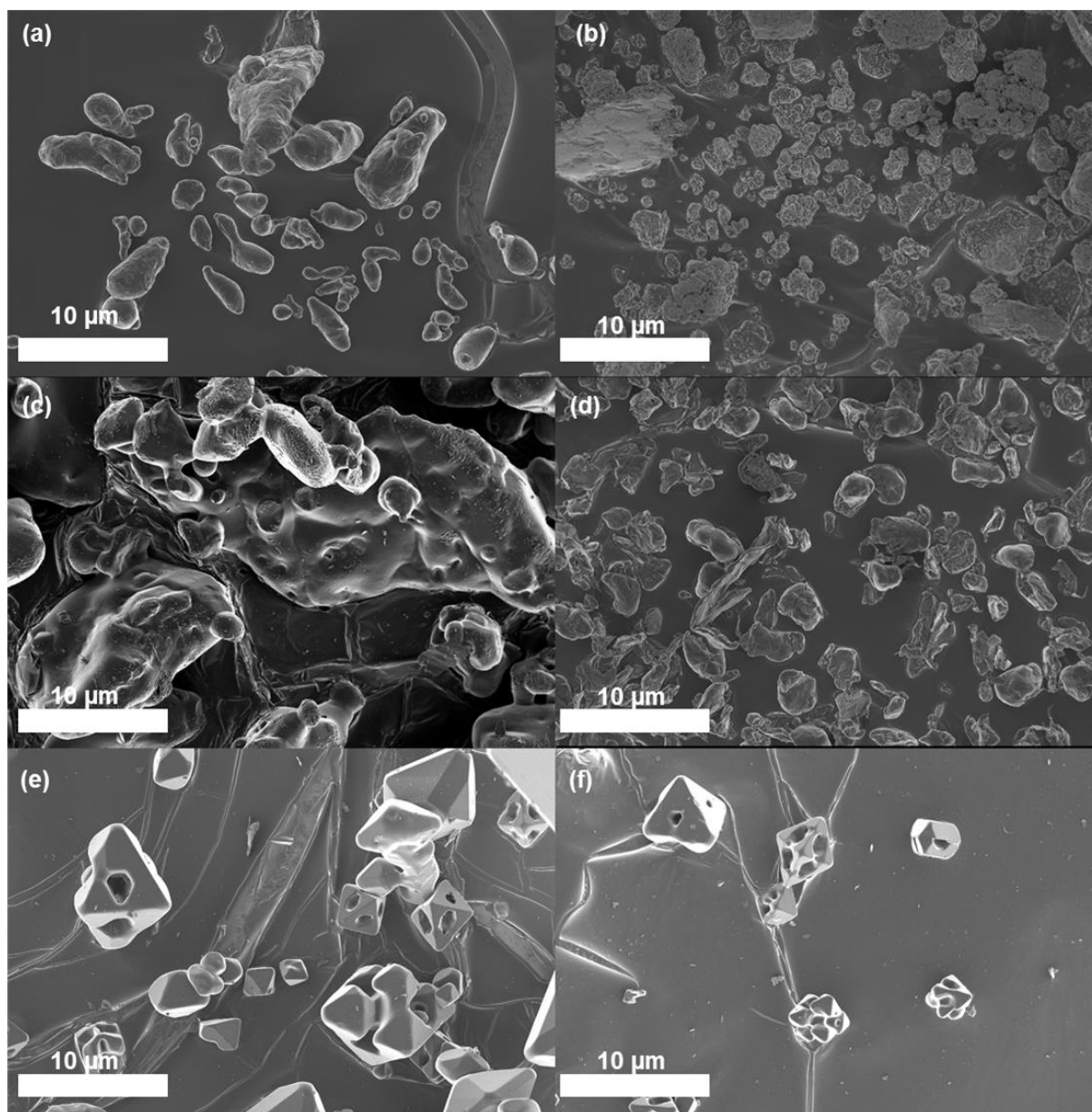


Figure 4-1. SEM imaging for the individual components used in the composition. (a) Aluminium, (b) copper oxide, (c) sulfur (d) PTFE and (e-f) recrystallized potassium periodate.

The aluminium particles shown in the Figure 4-1 (a) have a teardrop like structure. The particle size varied somewhat with the smallest particles being in the region of 1 µm while the larger ones exceed 10 µm in size. The sulfur particles, Figure 4-1 (c), had a similar shape to that the aluminium but appear to be larger. Copper(II) oxide apparently comprised two different structures. Larger flake-like structures with agglomerated clumps of material scattered in-between are seen in Figure 4-1(b). The smaller PTFE particles tended towards a spherical

shape while a few larger ones had rod- or flake-like shapes. The potassium periodate, as recrystallized from solution, featured a relatively homogenous particle size and structure as seen in Figure 4-1 (e-f).

The composition produced by recrystallizing the potassium periodate in the presence of aluminium was imaged by optical microscopy. An example of this product is shown in Figure 4-2.

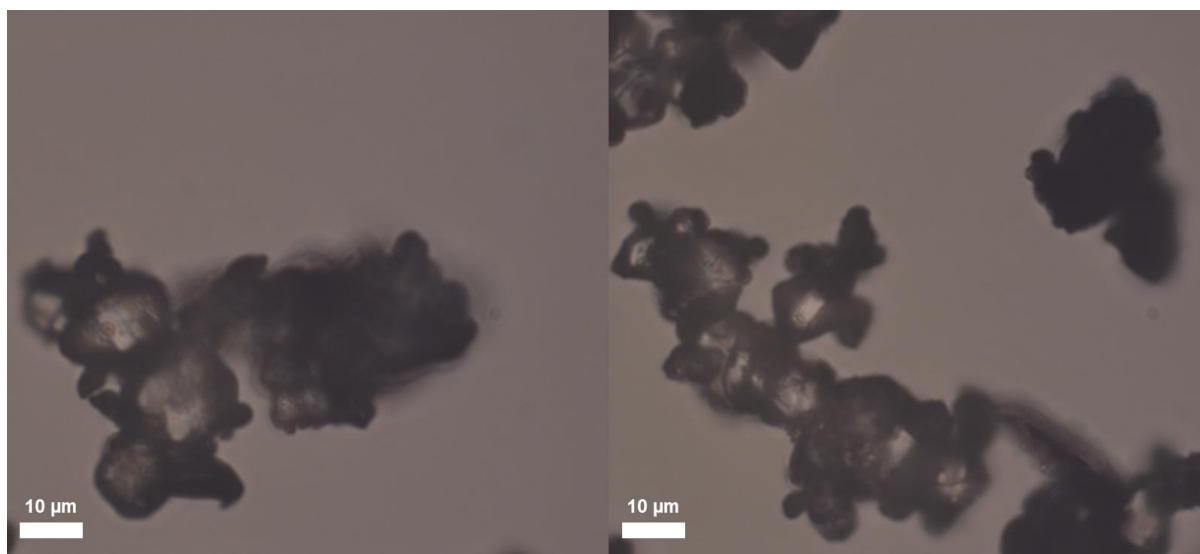


Figure 4-2. Optical microscope images of potassium periodate recrystallized in the presence of aluminium.

Figure 4-2 shows agglomerates of aluminium with potassium periodate. The potassium periodate crystals are easily identified by comparing this image with that of Figure 4-1. It indicates that the recrystallization resulted in at least some adhesion between the aluminium and the potassium periodate.

4.3 XRD and XRF results

The XRD diffractograms and XRF analysis are presented in Appendix A. The XRF and XRD results confirmed that all of the components used in the trials were of high purity. It is believed that the trace elements that were detected are unlikely to have had any noticeable impact on the performance of compositions.

4.4 Iodine test

The iodine test was done in order to determine whether the wet mixing process could have led to the reduction of the iodate. If such unwanted reactions happened, the fuel or oxidiser

quality would have been impacted. The addition of potassium iodide to a solution of potassium periodate produces the red orange solution seen in Figure 4-3 (a). The solution is at its darkest close to the surface of the undissolved potassium periodate particles. The addition of the potassium periodate to a dextrin solution causes no change in colour as seen in Figure 4-3 (b) owing to the absence of the triiodide ion. The addition of potassium iodide solution in (b) caused an immediate change to a deep purple colour (c).

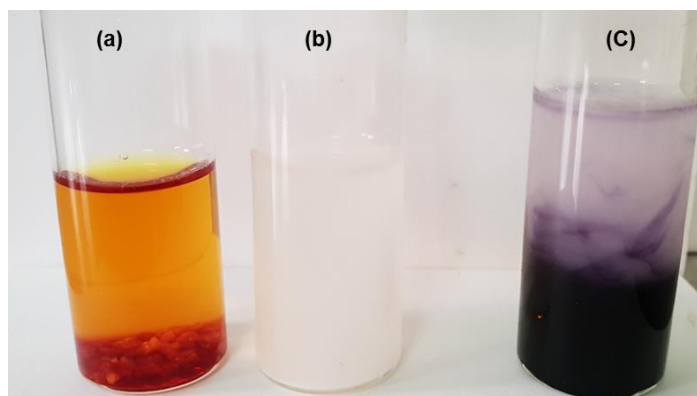


Figure 4-3. Demonstration of the iodine test without aluminium present. (a) Contains a KIO_4/KI solution, (b) contains a $\text{KIO}_4/\text{dextrin}$ solution, and (c) contains $\text{KIO}_4/\text{dextrin}/\text{KI}$.

This process was repeated under the same conditions as was used when mixing the aluminium and potassium periodate in order to determine if the aluminium is oxidised by the potassium periodate solution. The four sample sets collected are shown Figure 4-4. The addition of dextrin only did not trigger a colour change. However, addition of the potassium iodide to a solution containing dextrin and the potassium periodate did trigger a colour change to a dark red.

The dextrin content was increased after 20 minutes by adding an additional 2 mL of the solution to each of the vials. This resulted in a shift to the purple colour as seen in the second column of Figure 4-4. The final row of the Figure contains four vials. The final vial, furthest to the right, in each image contains only the mixing solution and potassium iodide. Indicating that the colour change witnessed for the vials containing dextrin was due to an interaction between it and triiodide that formed in solution. Iodine gas is released when the solution contains both potassium periodate and potassium iodide. This is seen in the bottom row of vials where a purple substance can be seen accumulating at the cap.

The results of the iodine test show that the potassium periodate solution does not produce the triiodide ion in noticeable quantities when in prolonged contact with the aluminium. This indicates that the aluminium does not reduce the potassium periodate in solution according to

Scheme 3-8. This is not to say that no reaction taking place, other reactions might have occurred but their rate might have been slow. Further studies are required to confirm that the fuel is not affected by this mixing method.

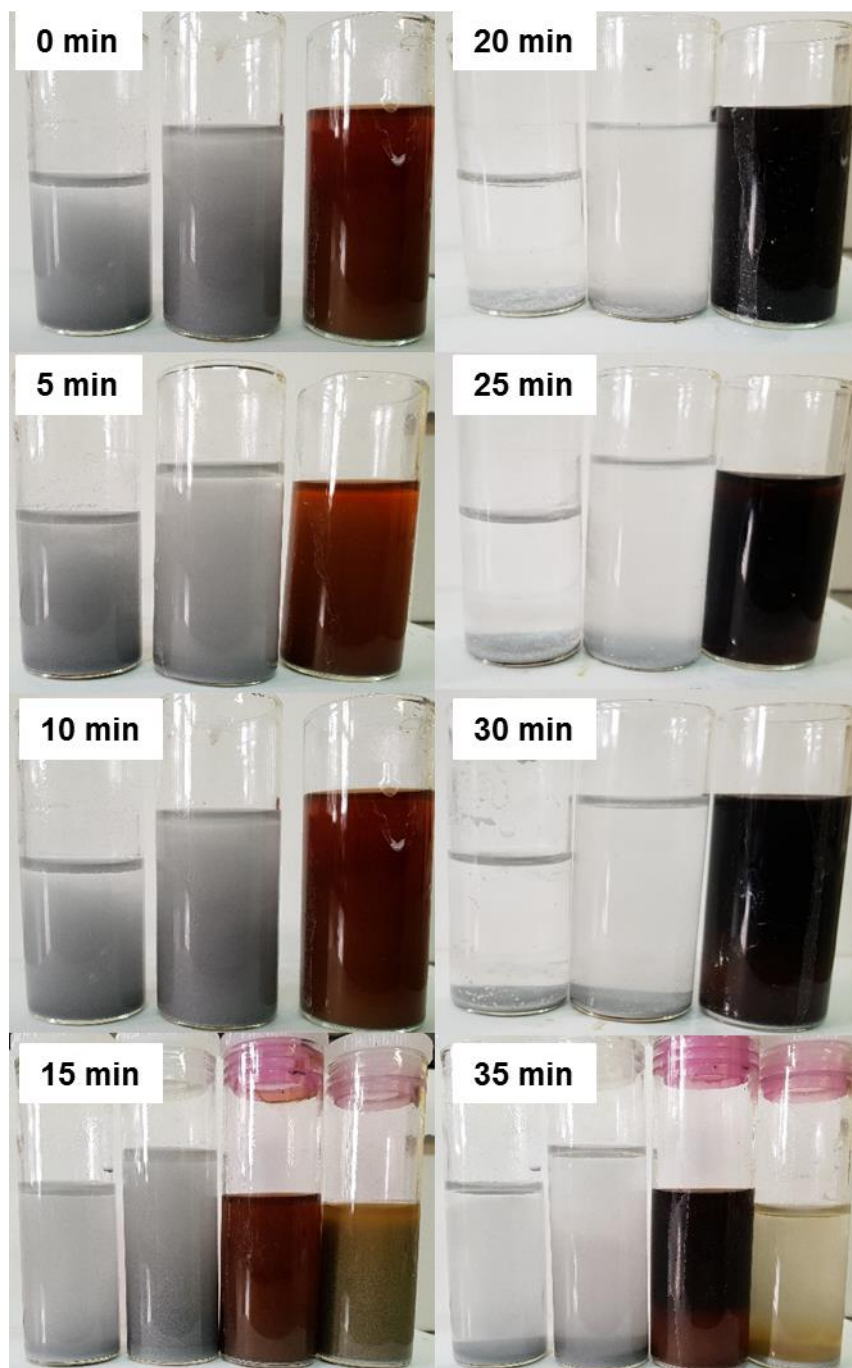


Figure 4-4. Iodine test results. The vial contents at each interval are: (Left) Al/KIO_4 , (middle) $\text{Al/KIO}_4/\text{dextrin}$, (right) $\text{Al/KIO}_4/\text{dextrin/KI}$ and (far-right) $\text{Al/KIO}_4/\text{KI}$.

4.5 DTA analysis

Thermal analysis is a useful tool for determining the ignition temperature of a composition. It can also provide insight into the reaction mechanisms at work. In the following discussion the DTA responses of the materials will be shown. Exothermic events result in peaks that are presently indicated by a rise above the baseline while endotherms drop below it.

Identifying the ignition temperature in the context of the DTA can be difficult when there are multiple exothermic events. The ignition temperature corresponds to the point at which an immediate self-propagating exothermic reaction occurs (Conkling and Mocella, 2019). A DTA exotherm, that presents itself as a rapid and significant deviation from the baseline, is most likely caused by an ignition event. This is referred to as a thermal runaway. This event tends to produce a strong exothermic response that shows up as a looping structure, due to the furnace controller failing in its attempt to maintain the temperature rise within the furnace to the programmed value.

4.5.1 Aluminium oxidiser combinations

The constituent components of the compositions were the first to be analysed. This was done to identify melting, decomposition and other phase transitions that may affect the reactivity of the compositions. The thermal responses for the base components are shown in Figure 4-5.

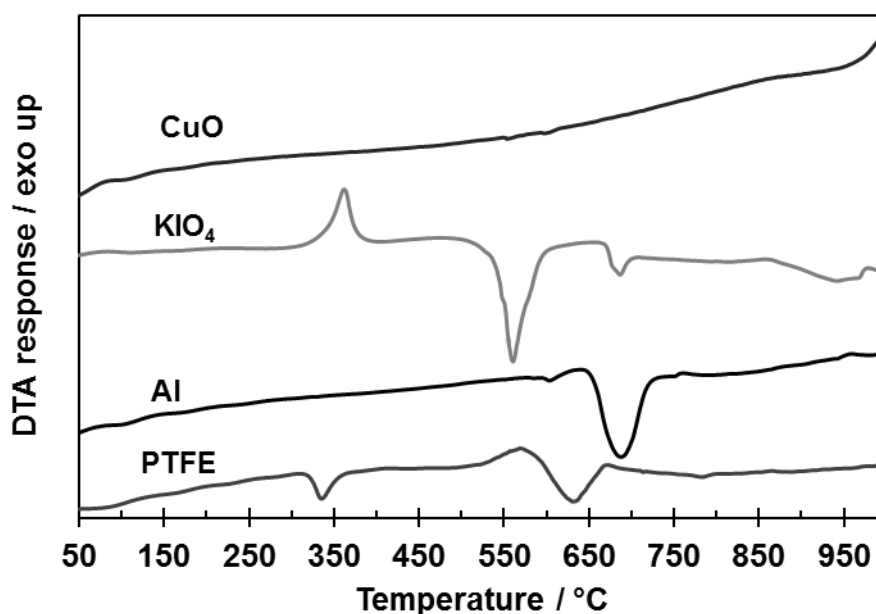


Figure 4-5. DTA response for single components.

Figure 4-5 indicates that copper(II) oxide is the most thermally stable oxidiser. Copper(II) oxide is only active at elevated temperatures (Topnani et al., 2010, Chadda et al., 1989, Hu et al., 2016, Umbrajkar et al., 2006). The results shown in the Figure are comparable to the literature values listed in Table 2-6. Copper(II) oxide has a two stage decomposition process. It first decomposes to copper(I) oxide (Cu_2O) releasing oxygen in the process. This process is represented by Scheme 4-1 (Chadda et al., 1989).



This process occurs in a range of 760 °C to 910 °C (Chadda et al., 1989). The second stage of its decomposition occurs at even higher temperatures. Potassium periodate also experiences a two stage decomposition process. This is shown in Scheme 4-2 and Scheme 4-3.



Both of these stages are evident in Figure 4-5. The first is represented by an exotherm while the second is an endotherm. The initial stage of decomposition, as indicated by Scheme 4-2, starts in the region of 350 °C. This exothermic decomposition of the potassium periodate to potassium iodate (KIO_3) releases some oxygen which can be utilised with the right fuel selection. The endothermic peak around 550 °C is indicative of potassium iodate decomposing (Jian et al., 2013, Zhou et al., 2017, Oxley et al., 2015, Muraleedharan et al., 2010). The net result of the complete decomposition is an endothermic process. The last deviation from the baseline occurs at approximately 680 °C. This endotherm is due to the melting of the potassium iodide (KI) that formed as a result of Scheme 4-3.

PTFE starts melting at 320 °C (Blumm et al., 2010), and its bulk mass loss onset has been reported as approximately 560 °C (Puts and Crouse, 2014). These events are both visible in Figure 4-5. The melting process is represented by the endotherm while the decomposition is more complex. It has an initial exotherm followed by an endotherm and smaller peak which may be an exotherm or a slight overcorrection to the new baseline.

In the inert atmosphere provided to the furnace, the only response one could expect to see for aluminium was a melting endotherm. Phase changes within the alumina surface layer would occur as well. It would however not show up in the data due to the relatively low alumina content of the aluminium sample.

With the responses of the individual components known, the process was repeated for binary mixtures. Figure 4-6 depicts the DTA responses for the three aluminium-fuelled compositions.

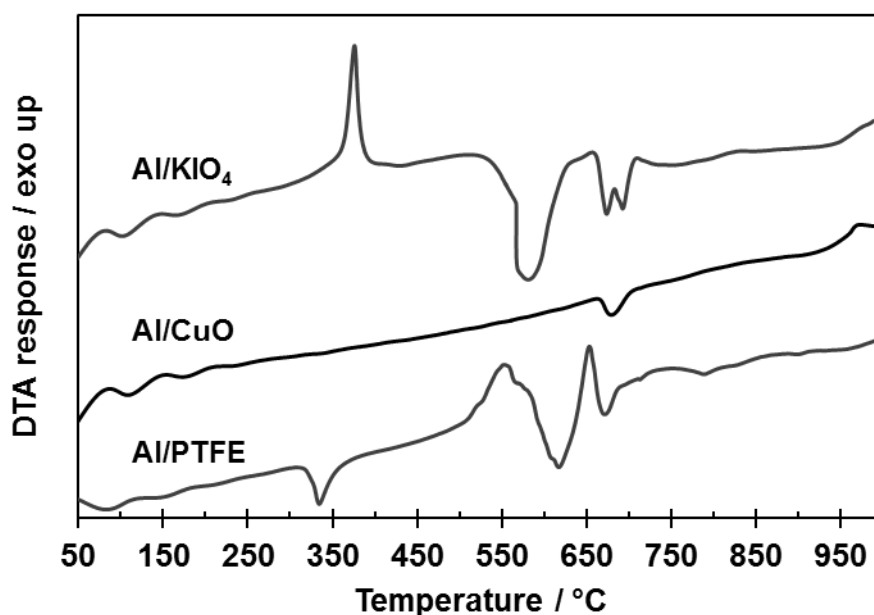


Figure 4-6. DTA responses for binary systems.

The responses for the aluminium and copper(II) oxide system was similar to the response for neat copper(II) oxide in Figure 4-5. However, it features an endothermic peak at 660 °C, which corresponds to the melting temperature of aluminium. There is no evidence for a thermal runaway. An ignition exotherm was expected to commence at around 950 °C as was demonstrated by Ilunga et al. (2011).

A similar uneventful response was recorded for the aluminium potassium periodate combination. The responses for this composition were the same as those of the individual components, i.e. there was no evidence of an ignition exotherm. It was expected that ignition would occur around 627 °C. This is where the alumina layer on the aluminium particles phase-changes from amorphous to γ -alumina (Zhou et al., 2017). This lack of a thermal runaway was not entirely unexpected as this composition has ignition difficulties in certain environments (Jian et al., 2013, Zhou et al., 2017). It is most likely caused by the relatively low decomposition temperature of the potassium periodate. It is well below the temperature where aluminium is considered reactive. In an environment like the one of the DTA ignitability of the sample may be reduced. The reasons for this are twofold and attributable to sample size and the inert atmosphere. The oxygen released by the decomposing potassium periodate is diluted or removed from the immediate surroundings before a self-sustained reaction can occur with the

aluminium. The small sample size further inhibits the process as the removal of components from the composition will have a larger effect on the heat build-up within the sample compared to a larger sample. Either one or both of these aspects might be the cause of the lack of visible exothermic response for the composition.

The PTFE binary system has an exotherm starting below 500 °C. The exothermic pre-ignition reaction between PTFE and the alumina shell takes place above 400 °C and produces aluminium fluoride, see Chapter 2.7.3. The next exotherm occurs at the temperature where one expects the aluminium melting endotherm. It corresponds to the reaction between the aluminium and the fluorine-containing species produced by the PTFE decomposition. For the binary systems, the only clear evidence of a reaction was seen for the PTFE-based system. This was most likely due to the ability of fluorine to interact with the alumina layer on the aluminium. These reactions do however not bear the hallmarks of thermal runaway.

Blends were made between the potassium periodate-based binary and the other binary compositions. This was done to investigate the possibility of favourable interactions between the oxidisers that would lower the ignition temperature. The DTA responses for these systems are displayed in Figure 4-7 and Figure 4-8.

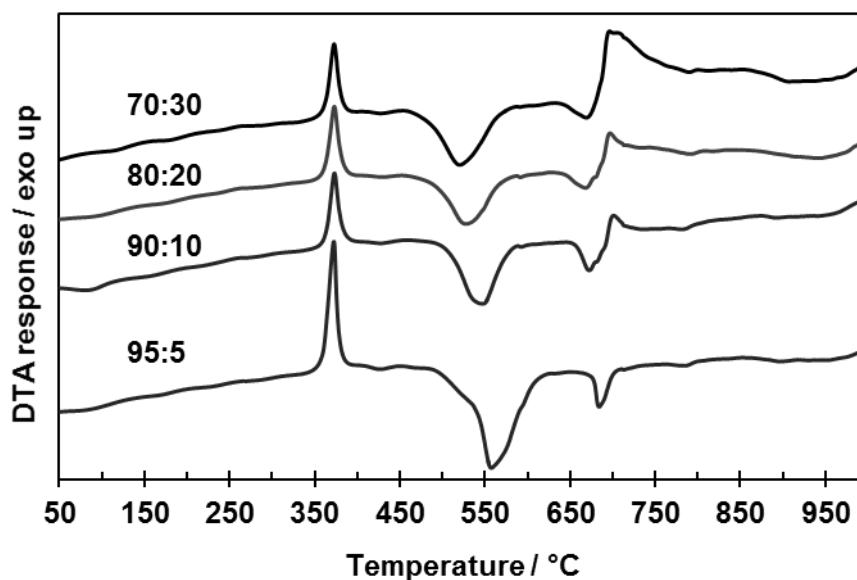


Figure 4-7. DTA responses for the Al/KIO₄ composition with the addition of the Al/CuO composition at different mass ratios [Al/KIO₄ : Al/CuO].

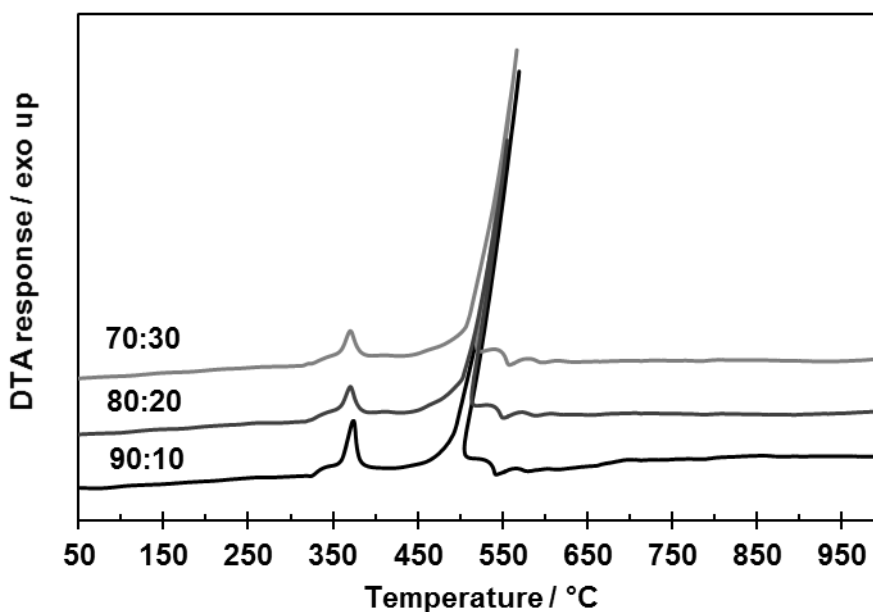


Figure 4-8. DTA responses for the Al/KIO₄ composition with the addition of the Al/PTFE composition at different mass ratios [Al/KIO₄ : Al/PTFE].

Figure 4-7 illustrates an apparent catalytic interaction between the copper(II) oxide and the potassium iodate which formed when the periodate decomposed. Increased loading of copper(II) oxide thermite lead to a lowering of the decomposition onset temperature. The lowest onset temperature was about 480 °C, i.e. a reduction of approximately 30 °C from the onset seen for pure potassium periodate response reported in Figure 4-5. This interaction between potassium periodate and copper(II) oxide was previously documented by Patel and Bhattacharya (2017). This interaction may prove to be problematic in some situations as the aluminium might not have reached a temperature at which it is able to react with the released oxygen. For example, in the present instance the catalytic effect did not contribute to a visible reduction in the ignition temperature of the base system. The melting endotherm for aluminium was followed by an exotherm. The location of this broad exotherm possibly obscured the melting endotherm of the potassium iodide. Figure 4-9 proves that this exotherm is not attributable to a reaction between the two oxidisers. Therefore, the implication is that it was due to a reaction between the aluminium and oxygen rather than an interaction between the copper oxide and potassium iodide. Furthermore, it is at its most prominent at higher contents of the Al/CuO thermite. The location did, however, remain more or less fixed throughout the composition range.

The first evidence of a thermal runaway is indicated in Figure 4-8. Since thermal runaway was not present in the DTA responses for the PTFE-containing binary composition or that of the base composition it would imply a different reaction mechanism was at work. Unlike the effect witnessed for Al/KIO₄/CuO compositions, the event did not appear to depend on the PTFE content. This is because thermal runaway always initiated in the range of 480 °C to 490 °C irrespective of the composition ratios tested. This is lower than the bulk mass loss onset temperature for PTFE and also lower than the expected ignition point for this base binary system.

A similar decrease in ignition temperature was recorded for the aluminium potassium perchlorate (KClO₄) thermite when adding aluminium fluoride. Freeman and Anderson (1966) found that a pre-ignition reaction occurred between the perchlorate and the aluminium fluoride resulting in the formation of potassium-aluminium fluoride. Direct addition of this compound to the thermite resulted in a 130 °C reduction in the ignition temperature (Freeman and Anderson, 1966). In an attempt to prove the existence of similar pre-ignition reaction, DTA analysis was performed on potassium iodide, potassium perchlorate-based systems as well as a set containing alumina instead of aluminium. The results of these runs are shown in Figure 4-9 to Figure 4-11.

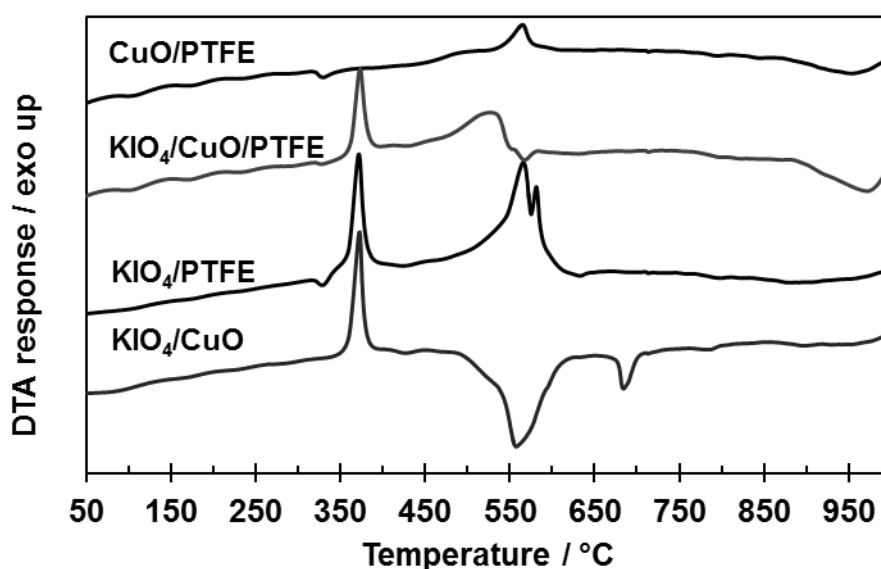


Figure 4-9. DTA responses for mixtures of the oxidisers.

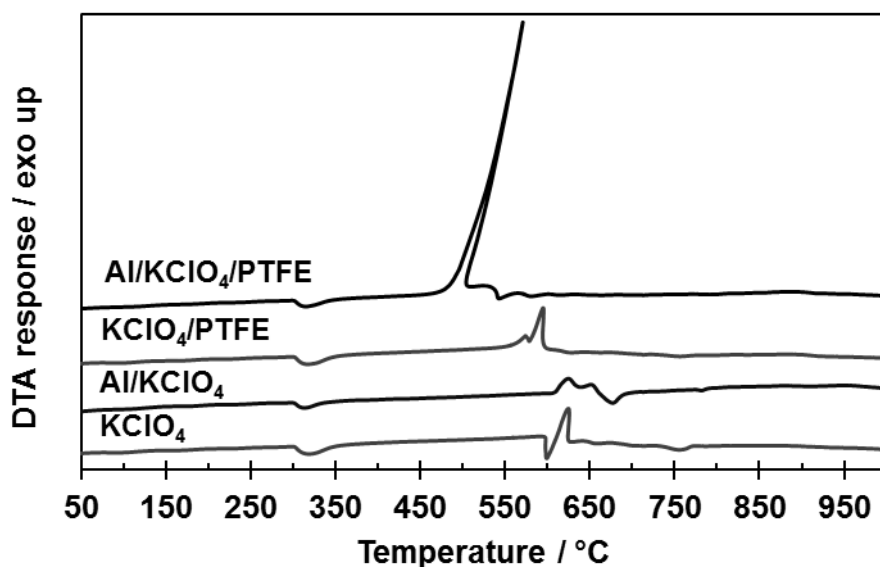


Figure 4-10. DTA responses for systems containing potassium perchlorate.

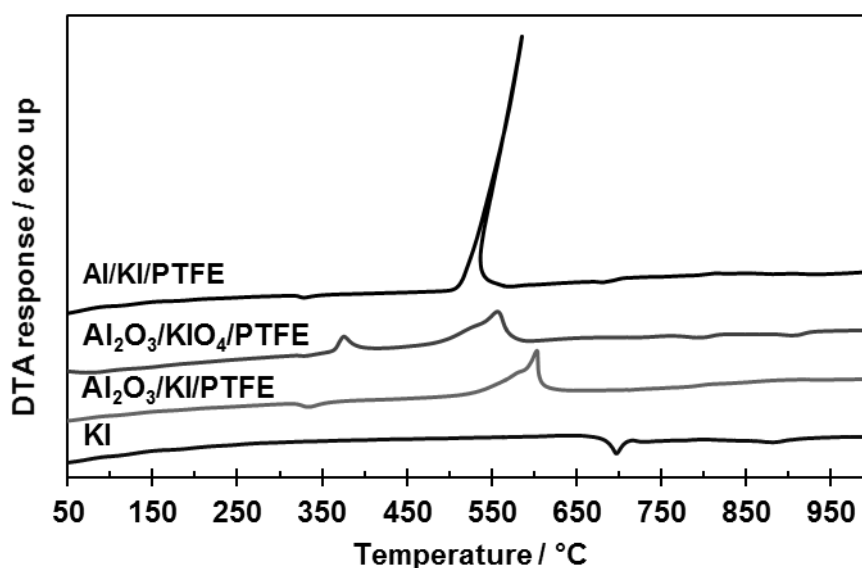


Figure 4-11. DTA responses for systems containing alumina and potassium iodide.

The DTA responses for oxidiser blends provided some insight into what might be happening in the Al/KIO₄/CuO and Al/KIO₄/CuO/PTFE compositions. Figure 4-9 indicates that there are interactions between some of the oxidisers. The most obvious one is the reaction between PTFE and potassium periodate. Adding copper(II) oxide to this mix appeared to have a catalytic effect that shifted the exotherm event to lower temperatures. The reaction between potassium periodate and PTFE is exothermic in nature. It is most likely occurring between the solid potassium iodate and the liquid formed during decomposition of the PTFE. The broad exotherm which starts around 480°C provides evidence for this. It commences at a

temperature that is lower than the bulk decomposition temperature of PTFE. It also extends beyond the region over which one expects to see the decomposition endotherm of potassium iodate. This is the same starting point as the thermal runaway witnessed in Figure 4-8. Its position also makes the presence of oxygen from the initial decomposition of potassium periodate unlikely. Furthermore, the melting endotherm of potassium iodide is absent suggesting that it did not form in sufficient quantities to affect the DTA response.

This suggests that the increased reactivity might be attributable to the formation of a potassium-aluminium fluoride complex. Support for this hypothesis is provided by the similar response witnessed in Figure 4-10 for a perchlorate containing system. As with the other binary systems, no thermal runaway occurred in the aluminium potassium perchlorate binary composition. PTFE and potassium perchlorate also reacted generating the exotherm seen in the DTA response shown in Figure 4-10. However, adding PTFE to the aluminium potassium perchlorate composition resulted in a thermal runaway. This event was initiated at a temperature of approximately 480 °C. The exotherm, of this interaction, is 50 °C lower than the decomposition temperature of the potassium perchlorate. This may provide some support for the suggestion of a potassium-aluminium fluoride interaction being the cause of the increased reactivity. This compound has been reported to assist with the destructive removal of the aluminium oxide layer coating the aluminium particles (Freeman and Anderson, 1966). Improved reactivity is the expected outcome.

More evidence for the existence of a reaction between the decomposing potassium periodate, PTFE and alumina shell provided by Figure 4-11. It reports on compositions containing components expected to be present in the base composition as either minor contaminants or as reaction products. Thermal runaway was achieved in the aluminium, potassium iodide and PTFE system. This event occurred in a similar position to that shown Figure 4-8. The absence of the expected potassium iodide melting endotherm from the response indicates that it was consumed in the reaction.

Replacing the aluminium with alumina resulted in a response with exothermic events but without achieving thermal runaway. This was expected as alumina would be a poor “fuel”. The position of the exotherm for this reaction as well as the absence of the potassium iodide melting endotherm strengthens the argument for a reaction between the alumina shell with PTFE and potassium iodide.

Copper(II) oxide accelerates the decomposition of PTFE (Puts and Crouse, 2014). However, no real evidence of this is evident in Figure 4-9. There was, however, evidence for it lowering the onset temperature of the potassium iodate decomposition. For this reason it was decided to combine all three systems. The Al/PTFE composition was added to achieve a 5 wt.% loading in the systems originally containing 30, 20 and 10 wt.% of the Al/CuO thermite. PTFE was added in a minor amount since its impact on the system is insensitive to the amount present, unlike the situation for the copper(II) oxide. The resulting DTA responses are shown in Figure 4-12.

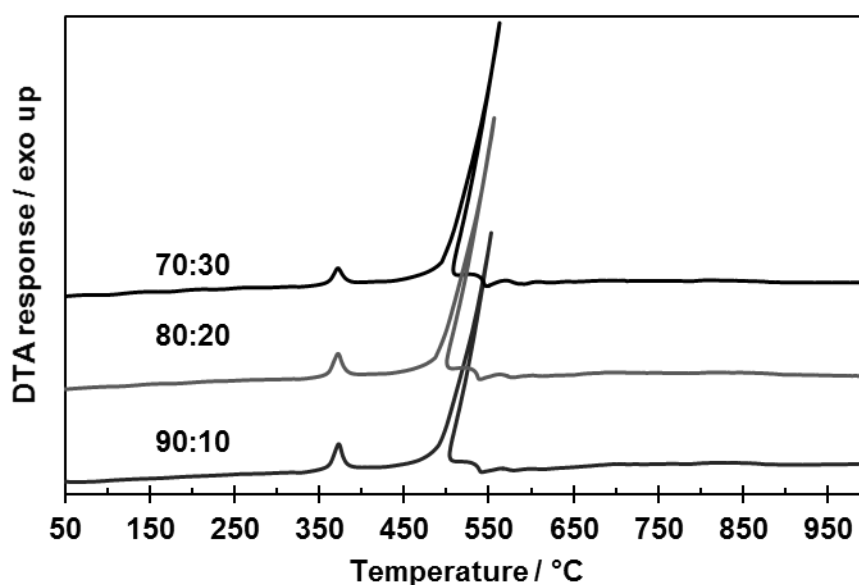


Figure 4-12. DTA responses for a combination of all three binary compositions. The ratios given are [Al/KIO₄ : Al/CuO] which is then further blended to contain 5 wt. % PTFE

Figure 4-12 shows a beneficial interaction when all three oxidisers are included. Thermal runaway was achieved in all three compositions. Furthermore, it occurred at a temperature lower than that found in Figure 4-8. The thermal runaway onset temperatures seen in Figure 4-12 are between 470 °C and 480 °C. This indicates the central role PTFE plays as a sensitising additive. By comparison, the presence of copper(II) oxide only decreased the onset temperature by approximately 10 °C in the ranges shown in Figure 4-12. The ignition temperatures in Figure 4-12 are as much as 150 °C lower than the values reported in literature for the base aluminium-potassium periodate system (Zhou et al., 2017, Zhou et al., 2015).

This dramatic decrease of the ignition temperature in Figure 4-12 suggests that there are alternative mechanisms at work. The first of these is likely the interaction between the oxidisers and the alumina shell protecting the thermite. The removal of which exposes the

aluminium which in turn can react with the oxygen released by the potassium periodate during its decomposition. Another possible interaction is the catalytic effect of copper oxide on the decomposition of PTFE and potassium iodate. Increasing the rate, or decreasing the decomposition onset temperature enhances the reactivity of the composition. Burn rate trials should contribute additional information regarding the effect the combination of the oxidisers has on the combustion performance of the system.

The base system, as well as two versions of the sensitised system, were subjected to further testing. From this point onward, the Al/KIO₄/CuO system refers to a blend of Al/KIO₄ and Al/CuO in a 90:10 mass ratio, while Al/KIO₄/CuO/PTFE refers to Al/KIO₄/CuO blended with the Al/PTFE composition at a 95:5 mass ratio.

4.5.2 Fuel combinations

It was mentioned in Chapter 2.7.2 that sulfur is used as a tinder in pyrotechnic compositions. For this reason it was also included in the trials. Figure 4-13 shows the DTA response for pure sulfur as well as its interactions with aluminium and potassium periodate.

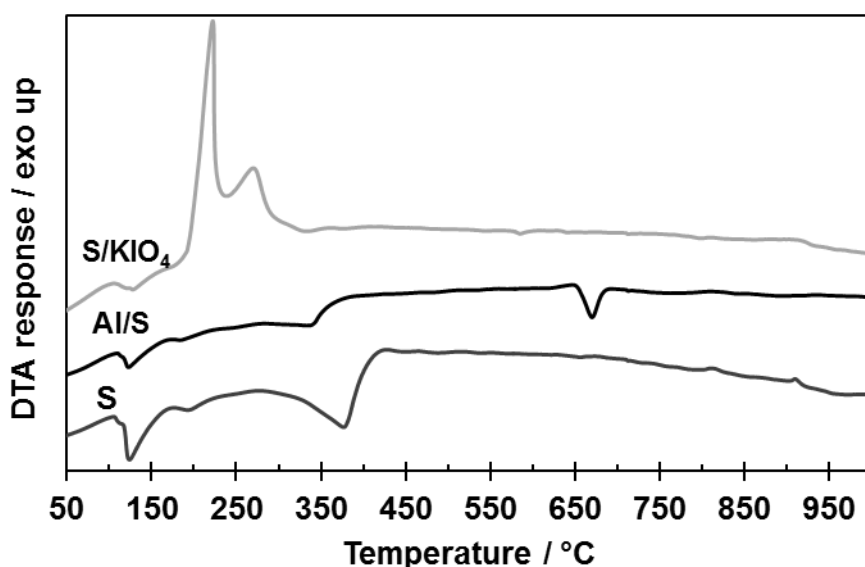


Figure 4-13. DTA response for sulfur and its binary compositions.

The DTA response for sulfur has an initial endotherm with a peak at a temperature of 125 °C and an onset at approximately 115 °C. This corresponds to the melting point of sulfur depending on the allotrope (Meyer, 1976). The second, larger endotherm starting at approximately 300 °C coincides with the onset of mass loss due to vaporisation (Vinayan et al., 2016, Wang et al., 2012)

The appearance of the response of the Al/S composition is similar to that for the neat sulfur. The only difference is the presence of the aluminium melting endotherm. The thermal response in Figure 4-13 provides no evidence for a reaction between sulfur and aluminium.

In contrast to the Al/S composition, the S/KIO₄ composition showed a strong exothermic response. The exotherm followed shortly after the melting of the sulfur in the composition. The thermal response indicates that most, if not all, of the potassium periodate was consumed in the reaction. This stems from the fact that the reaction occurred before the first stage decomposition of the potassium periodate and the absence of evidence for further decomposition processes in Figure 4-13.

Mixtures of the binary systems were investigated. The base Al/KIO₄ composition was combined with the Al/S and S/KIO₄ compositions in different ratios. The results are presented in Figure 4-14 and Figure 4-15.

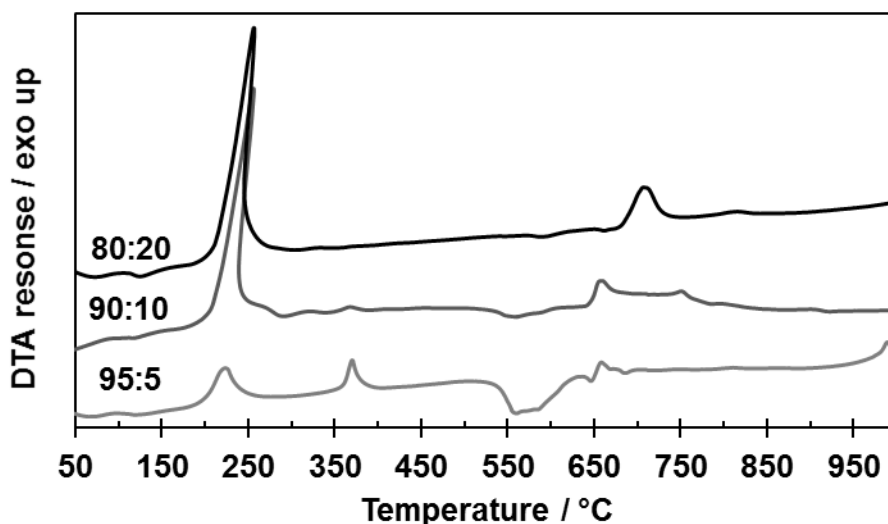


Figure 4-14. DTA response for an Al/KIO₄ composition combined with Al/S at different mass ratios [Al/KIO₄ : Al/S].

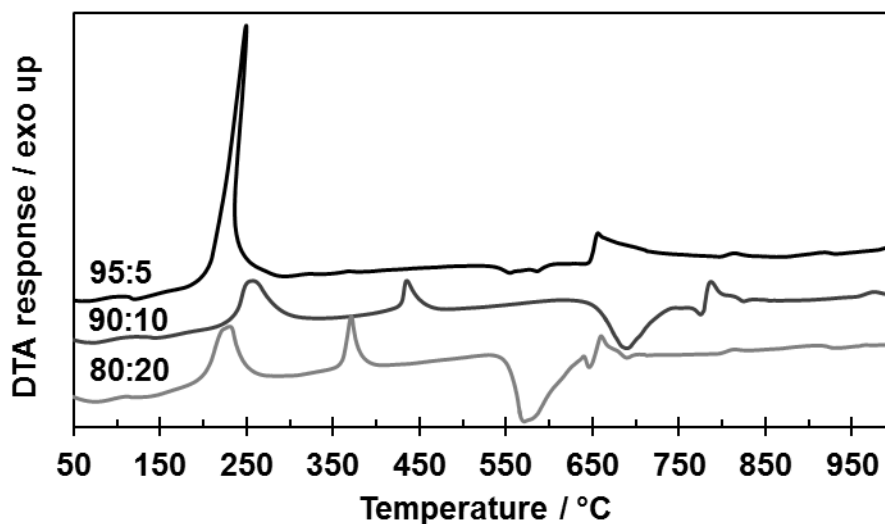


Figure 4-15. DTA response for an Al/KIO₄ composition combined with an aluminium and S/KIO₄ at different mass ratios [Al/KIO₄ : S/KIO₄].

The results indicate that the systems shown in Figure 4-14 and Figure 4-15 are significantly more sensitive to minor composition variations than that shown in Figure 4-7 and Figure 4-8. The manner in which sulfur was incorporated also drastically altered the response. The two systems acted somewhat inversely to each other. The Al/S composition dominated the DTA response at higher loadings. In contrast, the S/KIO₄ composition had a stronger effect at low loadings.

In all instances, an exotherm due to the reaction between sulfur and potassium periodate, and a second corresponding to the ignition of aluminium in the presence of oxygen, were present. This is unlike thermal response for the neat base composition for which there was no evidence for any reaction occurring. Perhaps the initial exothermic reactions, in the region of 200 °C, altered the aluminium surface chemistry, enabling it to react. This implies that the aluminium remains mostly “inactive” up to this point. Sulfur appears to assist the reaction between aluminium and potassium periodate. It does, however, not facilitate complete combustion of the aluminium at lower temperatures as was found with the addition of PTFE. At this point, the reason for the inverse response is not understood. However, it is speculated that it is due to a significant change in the ratio of potassium periodate present in the system. On adding the sulfur, in the form of a Al/S binary composition, the mass fraction of potassium periodate in the system decreases from 0.722 for the 95:5 mixture to 0.608 for the 80:20 mixture. Compare this to the corresponding change of 0.761 to 0.764 for the S/KIO₄-containing composition. It is likely that the higher potassium periodate loading begins to dominate the DTA response at the

higher loadings prevalent in the S/KIO₄ composition, thereby increasing the intensity of the periodate decomposition responses.

The effect of PTFE on the system was investigated by adding 5 wt. % of the Al/PTFE binary mixture to the sulfur-containing compositions. Two initial blends consisting of 90 wt. % Al/KIO₄ and 10 wt. % of Al/S or S/KIO₄ were used. The Al/PTFE composition was added to each of these blends. The resulting compositions were Al/KIO₄/S/KIO₄/Al/PTFE and Al/KIO₄/Al/S/Al/PTFE. The resulting DTA responses are shown in Figure 4-16.

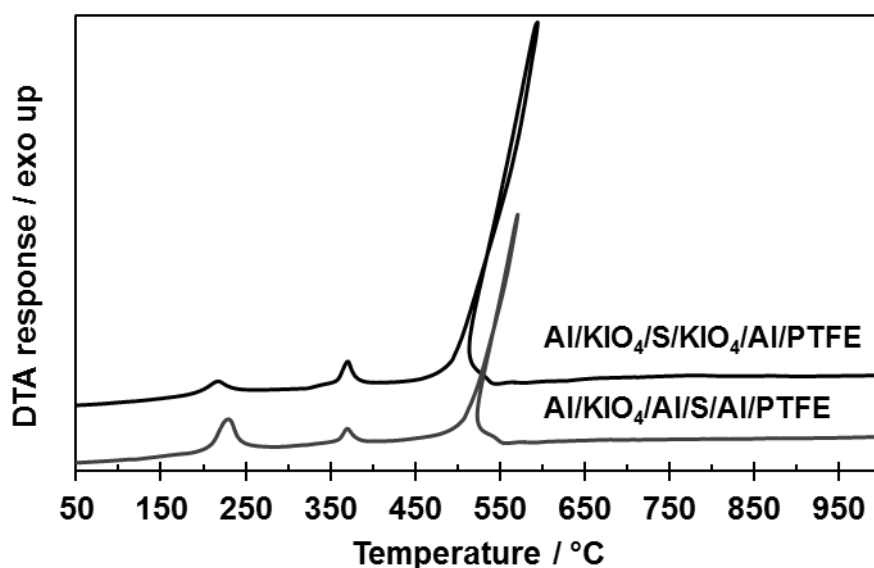


Figure 4-16. DTA response for the [Al/KIO₄:Al/S:Al/PTFE] and the [Al/KIO₄:S/KIO₄:Al/PTFE] blends mixed in a [90:10]:5 the ratio.

The addition of PTFE drastically changed the thermal responses of the systems. The first observation is the absence of the sulfur melt endotherm at 115 °C. This might be due to the lower of sulfur content compared to the systems in Figure 4-14 and Figure 4-15. Furthermore, in both instances, an exotherm occurs at the temperature at which potassium periodate decomposes. This exotherm is followed by a thermal runaway in both systems. This occurred at approximately 490 °C for the composition containing the S/KIO₄ composition, and 505 °C for the Al/S composition. The responses shown in Figure 4-16 are similar to those obtained in Figure 4-8 and approximately 20 °C to 35 °C higher than the extremes in Figure 4-12. It is clear that the addition of PTFE leads to thermal runaway and changes the response of both the 90:10 compositions. The lack of a strong initial exotherm as seen in Figure 4-14 and Figure 4-15 for the compositions mixed in 90:10 ratio may be due to a comparatively much stronger PTFE response. This implies that it is a scaling issue.

As mentioned, the system seems to be very sensitive to the overall sulfur content. Table 4-2 lists the ratios in which the binaries were combined as well as the final compositions reported in Figure 4-14 and Figure 4-16.

Table 4-2. Sulfur loading in the compositions.

Composition	Al (wt.%)	KIO₄ (wt.%)	S (wt.%)	PTFE (wt.%)	Total Fuel (wt.%)
[Al/KIO ₄]/[Al/S] (90:10)	25.2	68.4	6.4		31.6
[Al/KIO ₄]/[S/KIO ₄] (90:10)	21.60	76.22	2.18		23.78
[Al/KIO ₄]/[Al/S]/[Al/PTFE] (90:10:5)	25.27	64.98	6.08	3.68	31.35
[Al/KIO ₄]/[S/KIO ₄]/[Al/PTFE] (90:10:5)	21.85	72.41	2.07	3.68	23.92

The results shown in Table 4-2 illustrate the dilution effect of the Al/PTFE addition. The increased aluminium and PTFE present in the system make other pathways available and dilute the sulfur-potassium periodate response to some extent. The sulfur content is not the only cause for the large differences in the DTA responses. Combinations of factors, including the pre-ignition reaction mentioned in the previous section, contribute. Sulfur does appear to have a drastic effect on the DTA response of the base composition. But, as with the oxidisers shown previously, thermal runaway was only found for systems containing PTFE.

Sulfur was excluded from subsequent trials because its addition offered no clear advantage over the Al/KIO₄/CuO/PTFE composition described in Chapter 4.5.1. Furthermore, its responses are much more sensitive to minor compositional changes. This compositional sensitivity could potentially lead to unreliable results as minor differences in component distribution may occur for a variety of reasons. In addition, there are environmental concerns connected to the use of sulfur in pyrotechnic compositions which may limit its application in certain environments.

4.6 Sensitivity

Safe handling requires knowledge about more than just the thermal sensitivity of the energetic material. For this reason, the base composition as well as the sensitised composition were subjected to sensitivity testing. The results of these tests are compared to values for lead azide and lead styphnate in Table 4-3. It should be noted that the sensitivity values are strongly influenced by the crystal sizes of the high explosives listed (Klapötke, 2012).

Table 4-3. Comparing the ignition sensitivity of base- and sensitised composition to other explosives

Sample	Impact (J)	Friction (N)	ESD (mJ)
Al/KIO ₄	~ 52	>252	> 91.9
Al/KIO ₄ /CuO/PTFE	> 49	>324	> 28.4
Lead azide ¹	2.5-4	0.1-1	5
Lead styphnate ^{1,2}	3.4	<1	0.2
PETN	3 ¹ –5.1±1 ³	60 ^{1,3} –75.1 ⁴	62.5 ³ –600 ¹

(1)(Ilyushin et al., 2012) (Klapötke, 2012),(2) (Oyler et al., 2015), (3) (Lease et al., 2020),(4) (Künzel et al., 2017)

The addition of the additives had little effect on the impact sensitivity of the composition. The decrease in the friction sensitivity may be due to a lubricating effect provided by the PTFE (Conkling and Mocella, 2019). The addition of the Al/CuO composition to the base composition is the likely cause of the increased ESD sensitivity. Al/CuO compositions are reportedly more sensitive to ESD initiation than the Al/PTFE system (Weir et al., 2013).

4.7 Combustion performance and products.

4.7.1 Open burns

Preliminary open burns indicated dry mixing the Al/KIO₄ was insufficient to provide a reliable composition. Milling or grinding the potassium periodate to further reduce its particle size did not improve the ignitibility of the composition. A shift to the solution-based preparation method improved ignitibility to the extent that it could be ignited with G composition as the starter. The improved ignitibility was likely due to the intimate contact in the recrystallized composition. The Al/CuO and Al/PTFE compositions displayed no ignition problems when G composition was used as the initiator. Propagation was however an issue for the Al/PTFE composition, to the extent that accurate burn rate data could not be collected. The open burn results for the binary systems are displayed in Table 4-4.

Table 4-4. Open burn rates for binary systems

Composition	Open burn rate (cm·s ⁻¹)
Al/KIO ₄	16 ± 4
Al/CuO	221 ± 68
Al/PTFE	-

The Al/CuO composition had the fastest open burn rate. This was expected in view of the DTA results that indicated a condensed phase reaction, Section 4.5.1. The benefit of this is that the oxidiser is not lost to the environment before composition had sufficient time to heat up. The Al/KIO₄ composition had a much lower propagation rate when compared to the Al/CuO system. This may be due to the mismatch in the decomposition and ignition temperatures of the fuel and oxidiser. Since the oxygen released by the potassium periodate is diluted by the atmosphere surrounding the system, the stoichiometry of the composition is off. Furthermore, the loss of oxygen from the system, before ignition, also lowers the heat within the system thereby slowing down the reaction. As mentioned, the PTFE-based system ignited and propagated slowly for a short distance before dying out. A similar reliance on gas phase oxidising components is a likely explanation for the lack of propagation.

4.7.2 Combustion temperature measurements

The open burn temperature for 500 mg samples of the binary compositions as well as the Al/KIO₄/CuO/PTFE composition was determined using a pyrometer. The combustion temperature of the base- sensitised compositions were 2203 ± 36 °C and 2091 ± 19 °C respectively. It seems that the additives reduced the combustion temperatures. Both the binary compositions had lower combustion temperatures than the Al/KIO₄ system. They were 1100 ± 154 °C for the Al/CuO and 1524 ± 39 °C for Al/PTFE.

4.7.3 Closed burns

Confined burn rates are expected to be significantly faster due to the rise in pressure and the retention of the oxygen, see Equation 2-11. Table 4-5 lists the confined burn rates.

Table 4-5. Enclosed burn rate results

Sample	Average TMD (%)	Burn rate (m·s ⁻¹)
Al/CuO	35.2 ± 3.7	10.2 ± 1.7
Al/KIO ₄	45.5 ± 2.4	247 ± 43
Al/KIO ₄ /CuO	47.9 ± 2.0	425 ± 48
Al/KIO ₄ /CuO/PTFE	42.6 ± 3.7	593 ± 45

The Al/KIO₄ composition reacted significantly faster than the Al/CuO composition. It was expected that the Al/KIO₄ composition would produce more gaseous intermediates and products. The presence of more gaseous components should lead to a greater pressure build up within the burn tube. Evidence of greater pressures could be seen in the aftermath of the tests. The burn tubes shattered when compositions containing potassium periodate were used. However, the tubes used for the Al/CuO composition remained intact.

The Al/KIO₄/CuO composition burned significantly faster than the base composition. This increase is likely due to the catalytic effect of copper(II) oxide on the decomposition of the potassium periodate. This resulted in an increased rate of pressurisation within the tube. The Al/KIO₄/CuO/PTFE produced the fastest burn rate, more than double that of the base composition. This is attributed to the combined effects of sensitising the base composition to thermal ignition and a faster generation of gaseous species. The formation of aluminium fluoride can also provide an explanation since it should be in the gas-phase under these conditions, unlike the more stable aluminium oxides (Valluri et al., 2019). This has the benefit of increasing the system pressure whilst removing reaction inhibiting material from the aluminium surface.

Further evidence for pressure being responsible for the increased burn rates, is the observation that the burn rate was faster in the second half of the tube. This acceleration lead to an average burn rate of more than double that witnessed in the first half. In the case of the Al/KIO₄/CuO/PTFE composition the velocity increased from $445 \pm 33.4 \text{ m}\cdot\text{s}^{-1}$ to $889 \pm 67 \text{ m}\cdot\text{s}^{-1}$. Even though the burn speed in first stage of the Al/KIO₄/CuO system was $150 \text{ m}\cdot\text{s}^{-1}$ slower than that of Al/KIO₄/CuO/PTFE, it approached the same maximum speed in the second stage. The equivalence of the final burning speed might have be due to failure of silica tubes. The fracturing or rupturing of the tubes released combustion products relieving the pressure and thereby removing the driving force responsible for accelerating the reaction.

4.7.4 Calorimetry

Bomb calorimetry was performed on the compositions used in the enclosed burn trials. Table 4-6 has the results for the compositions used as well as the starter composition used in the trials.

Table 4-6. Average heat of reaction for pyrotechnic compositions used in burn trials

Composition	Heat of reaction (MJ·kg ⁻¹)
G	1.15 ± 0.01
Al/KIO ₄	6.64 ± 0.15
Al/CuO	4.07 ± 0.16
Al/PTFE	9.06 ± 0.22
Al/KIO ₄ /CuO	6.7 ± 0.18
Al/KIO ₄ /CuO/PTFE	6.84 ± 0.46

The additions made to the Al/KIO₄ composition had a very small impact on the heat of reaction. There was enough overlap of the results that the energy change can be considered negligible. Variance does increase with the complexity of the composition which may be indicative of minor differences in component dispersion in the bulk.

4.7.5 Burn residue analysis

The combustion products, recovered from the bomb, were analysed using XRD. The results are shown in Figure 4-17 and Table 4-7.

Table 4-7. Solid combustion products.

Composition	γ -Al ₂ O ₃ (wt.%)	KI (wt.%)	K (wt.%)	AlKO ₂ (wt.%)	CuI (wt.%)	(Cu(IO ₃) ₂) (wt.%)
Al/KIO ₄	21.78	78.22	-	-	-	-
Al/KIO ₄ /CuO	14.07	61.13	5.49	0.28	19.03	-
Al/KIO ₄ /CuO/PTFE	38.97	48.72	-	1.04	7.22	4.05

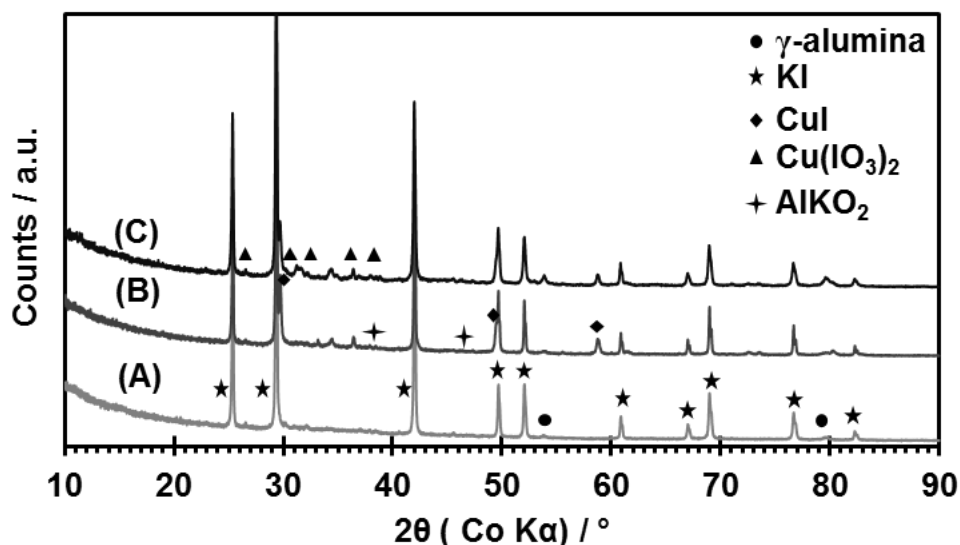


Figure 4-17. Diffractogram of combustion products from (A) Al/KIO₄, (B) Al/KIO₄/CuO and (C) Al/KIO₄/CuO/PTFE compositions.

The combustion products differ significantly from those suggested in the reaction schemes outlined in Chapter 3.2.1. The presence of the free potassium (K), copper(I) iodide (CuI) and copper(II) iodate (Cu(IO₃)₂) is an interesting occurrence. These compounds clearly form via other reactions between the reagents and intermediates. For example, copper does react with iodine and this reaction even occur at ambient temperatures (Elliott and Shelton, 1975). The formation of copper(II) iodate is interesting as it is itself a strong oxidising agent. It has been

studied as a source of iodine in biocidal compositions (Wang et al., 2015). This indicates that the reaction has either not consumed all of the aluminium or that under the conditions present other preferential (perhaps kinetically preferred) chemical pathways existed.

There is no evidence in Figure 4-17 for the formation of potassium-aluminium fluoride. This may imply that the drastic reduction of the ignition temperature, Section 4.5.1, may be due to different interactions. Alternatively, at the current PTFE content the resulting compound levels may be too low to register a clear response. Evidence for this can be drawn from the fact that no fluorine or carbon containing compounds were detected. The compounds formed with these two elements may also have been present in the gas phase when the solid combustion products were collected. Evidence for the formation of volatile components can be found by comparing the calculated feed ratios with those of the actual composition. The results of these calculations are shown in Table 4-8.

Table 4-8. Composition comparison between the as mixed and the calculated compositions from the burn residue assuming all components were accounted for in the analysis

Composition	Al (wt.%)		KIO ₄ (wt.%)		CuO (wt.%)	
	Mixed	Calculated	Mixed	Calculated	Mixed	Calculated
Al/KIO ₄	24	8.21	76	91.79	-	-
Al/KIO ₄ /CuO	23.4	5.64	68.4	88.37	8.2	5.99
Al/KIO ₄ /CuO/PTFE	23.55	22.26	64.98	73.67	7.79	4.07

The results indicate that only small part of the aluminium is accounted for in two of the compositions while the majority of the aluminium is present in the combustion products recovered for the Al/KIO₄/CuO/PTFE composition. Furthermore, back calculation of the potassium periodate content overestimates the actual feed ratio, while the copper(II) oxide feed is underestimated. Some sample is lost during the recovery process as gaseous components were vented to the atmosphere as the helium present in the bomb depressurised. Fine particulate matter could be seen leaving the bomb during the venting process. It should be clear that the combustion products listed in Table 4-7 are only part of the species produced during the reaction, and several other gaseous or solid species might have been present in all actuality.

4.7.6 Pressure measurements

Pressure measurements were made for the base, sensitised and G composition. Measurements on the G composition were necessary as it could potentially influence the data even though it burns in what is considered a gasless manner. Figure 4-18 shows an example of the data captured during these trials.

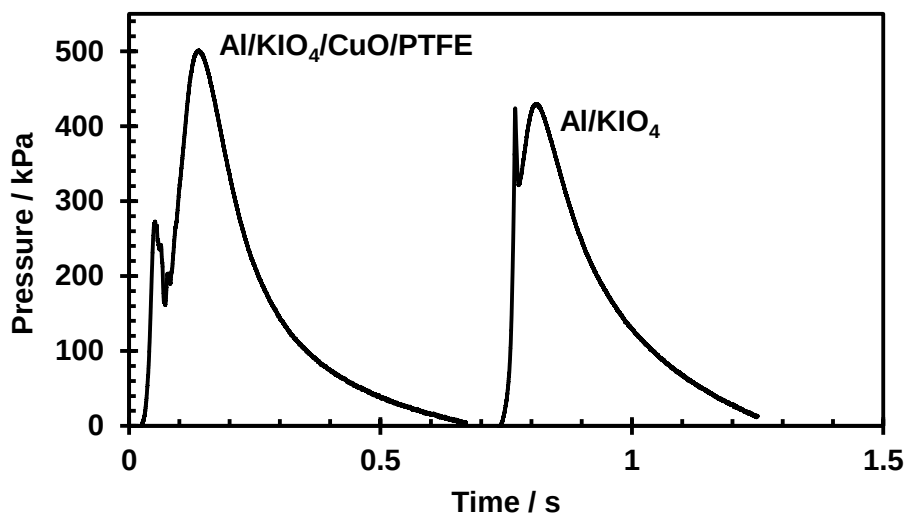


Figure 4-18. Pressure response for the compositions in air atmosphere.

The pressure responses featured a double peak when the runs were conducted in an air atmosphere. The reason for this was probably due to pre-ignition combustion due to the oxygen present in the air. To investigate this the same samples were run in an inert helium atmosphere. The results of which are shown Figure 4-19.

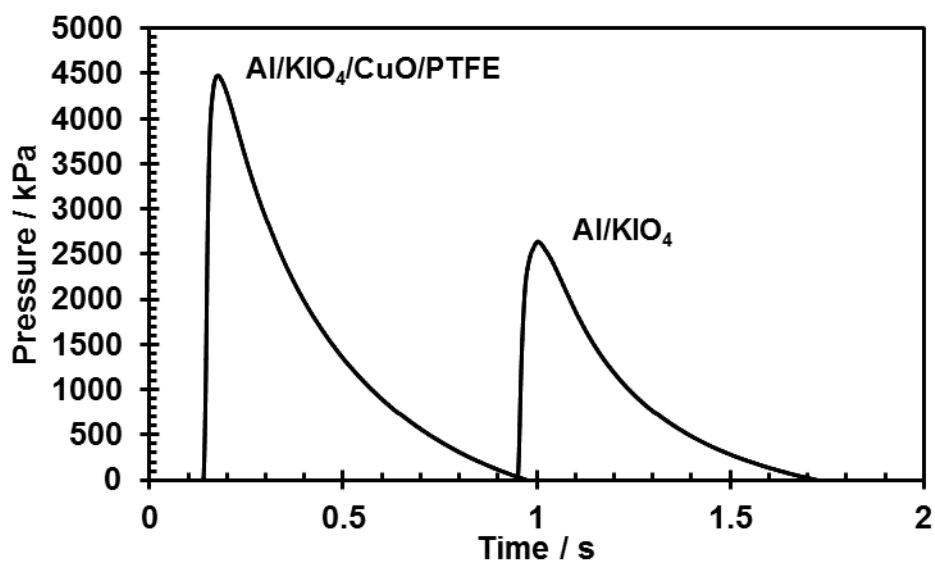


Figure 4-19. Pressure response for compositions in a 30 bar helium atmosphere.

The results shown in Figure 4-19 differ significantly from those seen Figure 4-18. This provides support for the hypothesis that the first peak was due to the presence of atmospheric oxygen. Furthermore, the overall pressure increase was significantly higher for the systems in the

pressurised helium atmosphere. Pressure measurements were made for G composition as well to confirm its stated gasless combustion. The results of these measurements are shown in Figure 4-20. In order to get reliable values for G composition, a larger mass was used. Approximately 1.2 g of G was necessary to achieve the responses shown.

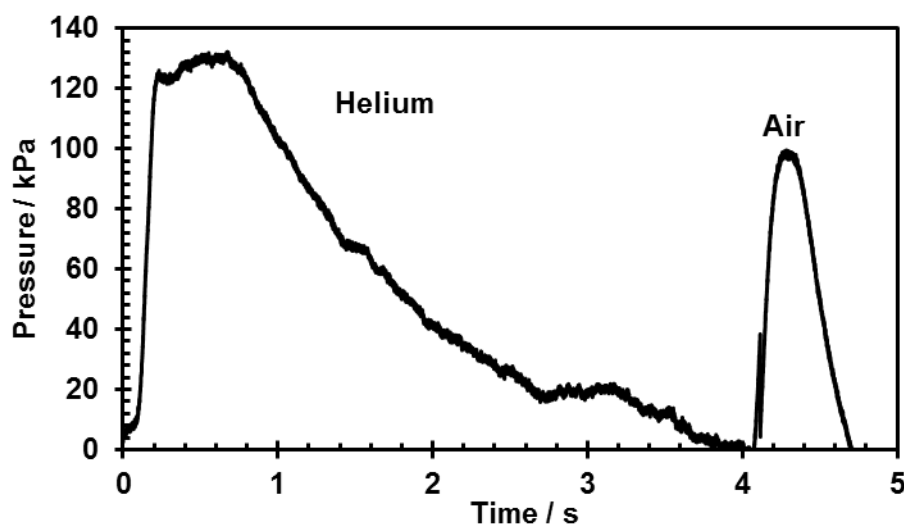


Figure 4-20. Pressure response for G composition in air and helium.

The results in the preceding Figures indicate that the G composition used to ignite the other compositions had a negligible effect on the pressurisation of the bomb. This was expected as it is intended to burn in a gas free manner. Table 4-9 provides detailed information on the pressurisation during the combustion trials. The pressurisation rate was determined according to the method described by Glavier et al. (2015). The initial peak pressure for the composition run in air and the overall maximum pressure are also shown. The average pressurisation rate was calculated from the start of pressure increase to the overall maximum pressure.

Table 4-9. Combustion pressure in air and helium

Sample	Initial peak pressure (kPa)	Maximum pressure change (kPa)	Max Pressurisation rate (MPa·s ⁻¹)	Average Pressurisation rate (MPa·s ⁻¹)
Air at atmospheric pressure				
Al/KIO ₄	397 ± 26	430 ± 9	52 ± 17	5.4 ± 0.9
Al/KIO ₄ /CuO/PTFE	253 ± 79	434 ± 62	37 ± 29	3.4 ± 0.9
Helium at 3 MPa				
Al/KIO ₄	-	2384 ± 288	167 ± 43	42 ± 12
Al/KIO ₄ /CuO/PTFE	-	4299 ± 318	369 ± 69	123 ± 18

The results shown in Table 4-9 indicate that the two compositions perform better in different environments. In air the Al/KIO₄ composition has a faster pressurisation rate and its overall maximum pressure is closer to that of the Al/KIO₄/CuO/PTFE composition. In contrast, in the helium environment, the Al/KIO₄/CuO/PTFE significantly outperformed the base composition from a peak pressure and pressurisation rate perspective. This increase in pressurisation rate is expected when the burning rate relationship is described by Equation 2-11. A higher initial pressure will increase the burning rate which in turn increases the rate of pressurisation and thereby further accelerating the burning rate. Interpretation of these results is difficult since the conditions under which these measurements were made differ greatly from the intended application and also from the experimental setup used by Glavier et al. (2015).

4.8 Detonator testing results

The initial trials were done in order to identify potential teething problems. These include packing stability, detonator shell failure and ignition problems.

4.8.1 Preliminary detonator assembly and tests

The intent of these tests were to identify potential problems with assembly and ignition before larger scale tests were conducted. Because of this, each detonator differed slightly as attempts were made to remedy the problems as they were encountered during the trials. The contents of the elements tested are displayed in Table 4-10. An example of an incrementally filled element is shown in Figure 4-21.

Table 4-10. Preliminary detonator assembly values

N	G (mg)	Height (mm)	Al/CuO (mg)	Height (mm)	Density (kg·m ⁻³)	Al/KIO ₄ (mg)	Height (mm)	Density (kg·m ⁻³)
1	100	10.2	100.8	4.63	1571	112.4	6.82	1190
2	50	4.1	162.3	8.85	1324	93.8	7.37	919
3	50	4.41	120.8	6.63	1315	114	9.96	1015
4	50	4.94	127	5.06	1811	206.9	15	996
5	50 + 20.2	4 and 2.15	120	5	1811	160	11.85	975

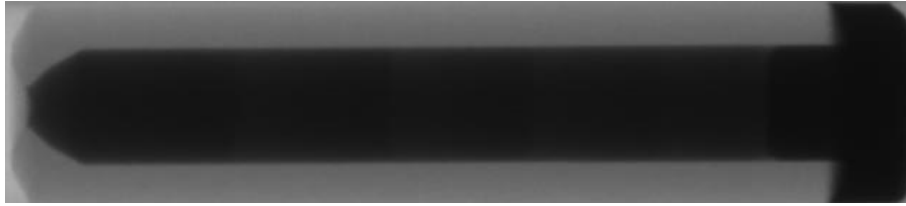


Figure 4-21. Delay element illustrating density variations in each increment. Increments were added from the right hand side.

The example shown above had increments loaded in equal masses and pressed with the same force. The increments can be identified by the shading transitions. The top part of each increment is darker while the lower portions are lighter. This illustrates the density variation within each layer of the composition. This is due to the manner in which the particles are consolidated during the pressing operation.

Detonators numbered 1 to 4 in Table 4-10 all failed to initiate prompting the changes seen in detonator 5. Changes were made based on inspection of X-ray images recorded afterwards. The images indicated that the combustion front failed to propagate past the initial layers. This is shown in Figure 4-22.

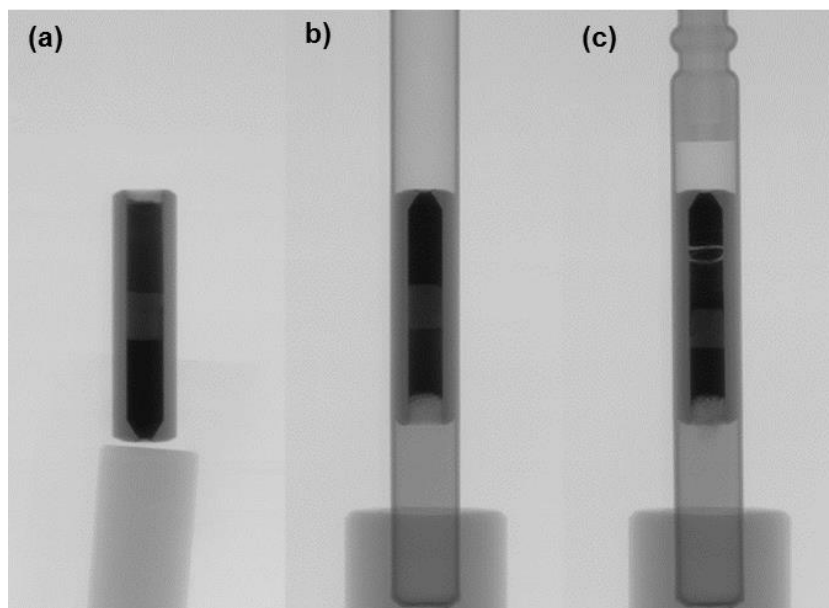


Figure 4-22. Detonator assembly, (a) loaded element (b) element in detonator shell and (c) evidence of the misfire.

The element in Figure 4-22 (a) shows the presence of three compositions: top Al/KIO_4 , middle Al/CuO (light grey in the image) and the bottom is G. The element pressed into the detonator shell is illustrated in (b). Discoloration is visible in the lower part of the element, this is due to

PETN being forced up into the column during the loading procedure. Initial analysis of the misfires proved to be difficult as the post burn evidence seen in Figure 4-22 (c) did not provide a clear representation of the burn event itself. From the image it would seem that separation occurred between the layers. In an attempt to identify the cause of this separation a detonator was loaded with an inert base charge and an element. The firing event of this element was recorded live with X-ray imaging. See Figure 4-23.

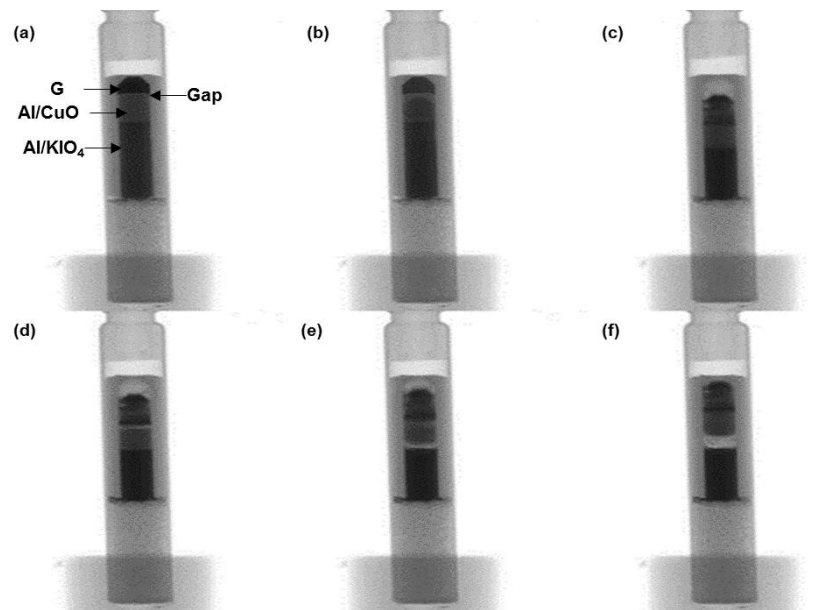


Figure 4-23. The movement of the composition during a firing event as monitored by X-ray imaging. (a) Initial state of the compositions. (b-c) Compression of the compositions due to shock tube output. (d) Composition layers separating. (e-f) composition rebounding back.

Recording the combustion event indicated that the composition moved during the combustion event. Figure 4-23 (a) shows the composition before ignition and its original stationary state. First, the composition was compressed by the pressure pulse imparted by the shock tube. This is seen in (b) and (c). The G composition separated from the copper oxide as shown in (d). Then in the following two images the column returned to its original position. Figure 4-23 (a) did however shine some light on a potential cause for the transition problems witnessed. The discoloration between the G composition and the Al/CuO composition either indicates a region of low density or a complete gap. G composition is considered to burn in a gasless fashion. This means that there is limited heat transfer between these two compositions when they are not in contact. This lack of contact could be the most likely cause for the ignition problems experienced. The gap was thought to form during the crimping process that was used to fix the shock tube to the detonator shell. This is shown in Figure 4-24 as well as the potential solution to the problem.

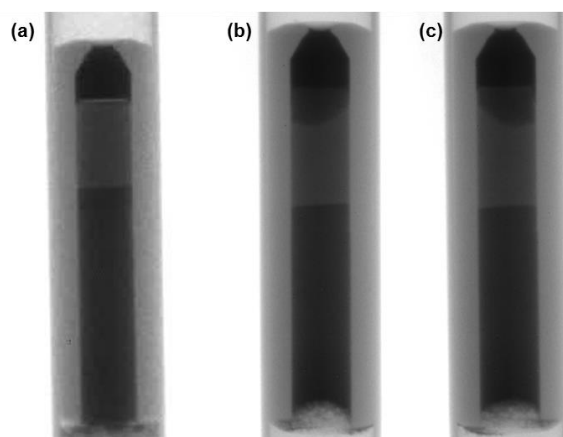


Figure 4-24. (a) Evidence of gap formation during crimping. (b) Pre-crimping of detonator containing and additional layer of loose G composition. (c) Post crimping of the detonator containing the additional G layer.

The gap formed between the first two compositions is clearly visible in Figure 4-24 (a). This gap formation is thought to be due to the fact that the pressed sample retains its shape and thereby positions better than that of the tap-filled compositions. In an attempt to counter this barrier effect, a mass of 20.2 mg of loose G composition was added onto the initial increment of G as seen in Table 4-10 run 5. The addition of this layer is also seen in Figure 4-24 (b) and (c). The loose G composition appears as a lighter shade of grey than that of the pressed G. A small gap or a region of very low density is still visible after crimping Figure 4-24 (c), however this did not prevent the burn from progressing to subsequent layers. Resulting in the first successful run. In this case the lower portion of the detonator shell was destroyed indicating that the composition did in fact, at the very minimum, burn through, see Figure 4-25.

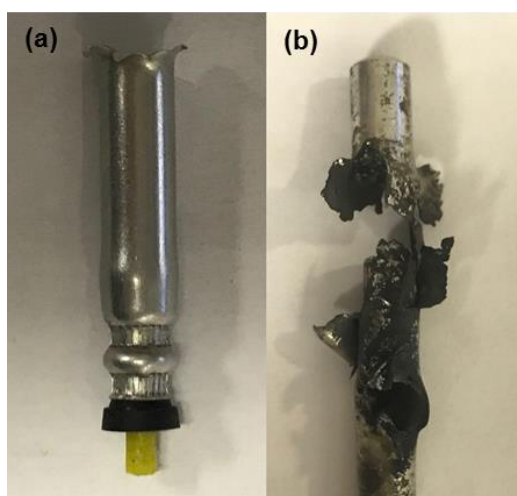


Figure 4-25. (a) Detonator shell remains from run 5. (b) Remains of a detonator shell that contained erythritol instead of PETN.

Further study is required to determine whether or not the PETN detonated. This is because the pyrotechnic composition by itself was able to destroy the detonator housing. However, there are differences in the damage seen in Figure 4-25. The detonator in (b) shows much charring unlike that in (a). This is most likely a burn residue from the erythritol. Furthermore, the damage is distributed across a wider area in (b). The reason for the difference in shell bursts shown may be due to the fact that PETN did contribute to the damage by partially reacting thereby increasing the pressure faster within the shell causing a more complete rupture. However, at this stage the situation is inconclusive.

4.8.2 Copper shells

Due to the failures, discussed above, the trials were repeated with copper shells together with the revised loading procedure described in Chapter 3.6.3. Figure 4-26 shows an example of an element loaded into the detonator shell, before and after crimping. Table 4-11 lists the loading parameters for all of the samples tested in the experiment.

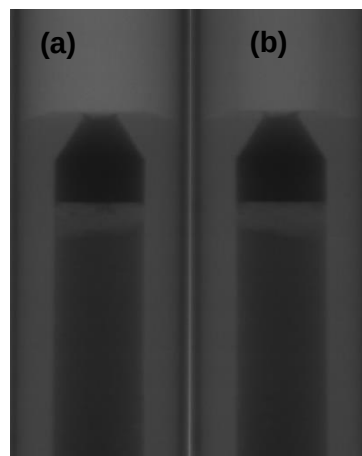


Figure 4-26. Detonator assembly before (a) and after (b) crimping.

Table 4-11. Loading parameters for copper detonator shells

Test	G (mg)	G (mg)	Al/CuO (mg)	Comp* (mg)	Comp* (mg)	Result
1	55	36	44	357	95	Fired
2	54	40	40	353	116	Misfired
3	57	35	43	341	98	Fired
4	57	34	45	352	105	Misfired
5	50	31	48	357	90	Fired
6	53	33	52	336	93	Fired
7	54	34	40	361	109	Fired
8	56	36	49	338	110	Fired
9	54	36	49	341	112	Fired
10	57	37	47	336	114	Fired
11	57	34	58	355	89	Fired
12	54	41	52	322	95	Misfired
13	54	37	41	346	88	Fired
14	51	36	57	344	94	Misfired
15	56	43	52	355	107	Fired

* Al/KIO₄/CuO/PTFE

The revised loading procedure did not develop the same gap that was seen previously. This may explain why the columns suffered fewer misfires than in the previous trials. Four misfires did occur, with no a priori evidence that the specific element could fail. X-ray imaging indicated that the shock tube failed to initiate G composition starter layers. In the cases where combustion of the composition did take place the detonator shell as well as the element failed before detonation could be initiated in the PETN column. Figure 4-27 provided evidence for this.



Figure 4-27. Copper shells post burn.

The remnants shown in Figure 4-27 (a) and (b) show the same premature failure as seen before with aluminium shells. This indicates that the copper shells were unable to contain the pressure in order to allow the PETN to burn to detonation. There was however one promising result in Figure 4-27 (c). In that instance the element suffered more damage than the other trials. This may be due to the influence of reacting PETN. Whether or not the failure shown in (c) occurred before, during or after the detonator shell failed is uncertain.

Due to the absence of evidence for the detonation of PETN, it must be assumed that the structural failure of the elements seen in Figure 4-27 contributed to the rupture of the outer shell. By comparing the damage to the detonator shell and the original position of the element within it one can deduce that the shell ruptured prematurely. Replacing the aluminium shells with copper shells did not provide sufficient reinforcement to protect the element or delay the rupture to allow DDT to occur.

4.8.3 Copper-nickel shells

The copper-nickel shells produced similar results to those found for the aluminium and copper shells. The shells ruptured prematurely with no verifiable evidence for detonation occurring. This was determined by using aluminium witness blocks and plates. The loading procedures and subsequent results are shown in Table 4-12 Figure 4-28 and Figure 4-29.

Table 4-12. Loading parameters for copper-nickel shells

Test	G (mg)	G (mg)	Al/CuO (mg)	Comp* (mg)	Comp* (mg)	Result
1	60	34	58	362	86	Fired
2	62	25	63	335	96	Fired
3	54	34	59	334	98	Fired
4	60	30	57	322	100	Fired
5	60	32	53	320	82	Fired

* Al/KIO₄/CuO/PTFE



Figure 4-28. Copper-nickel shells post burn.



Figure 4-29. Witness plate results from detonator trials. (Dents are circled)

The witness plates showed some evidence of thermal damage as well as denting where the detonator base made contact with it. The damage seen is not indicative of a detonation event occurring. A detonator firing correctly would cause significant cratering in the witness plate.

4.8.4 Flying plate detonator

The previous section illustrated the problems with confinement. In an attempt to accelerate the possible transition to detonation of the PETN base charge, a flying plate style detonator was investigated. The intention was to initiate a transition to detonation before the catastrophic failure of the detonator shell occurs. The aluminium elements proved to be unreliable for the composition being investigated. For this reason, steel was selected as material of construction

for the elements. The hope was that this would be able to resist the pressure within the combustion chamber. Furthermore, it was expected that the pressure build-up would be even higher with the FPD design, higher than was the case for the standard elements used up to this point.

Initial testing was conducted by loading the elements in the same manner as described in Section 3.6.3. The combustion chamber length was kept approximately constant. Two different element lengths (SB = 27 mm and LB = 29 mm) were used in order to allow for a variation in the barrel lengths. The 29 mm elements provided for longer barrel options. The chamber length was also varied with the 29 mm elements. Using a barrel length similar to that of the SB elements implies that the combustion chamber was slightly larger (LTSB). This also meant that the density of the composition in them was lower than that for LB style elements. Short elements were used in the final alteration (STHV), and the loading procedure was changed. The second increment of G composition was left out and the first increment of Al/KIO₄/CuO/PTFE was increased by approximately 30 mg. The contents of the element and maximum recorded velocities are reported in Table 4-13 and Table 4-14.

Table 4-13. Slapper elements loading and performance

Test	Total Mass (mg)	G (wt. %)	Al/CuO (wt. %)	Comp ⁺ (wt. %)	Barrel length (mm)	Peak velocity measured (m·s ⁻¹)
Short barrel						
SB3	644	14.91	9.01	76.07	3.9	407
SB4	632	14.72	8.54	76.74	3.9	398
SB5	650	14.31	9.54	76.15	3	410
SB6	648	14.51	9.26	76.23	3.9	420
SB7	642	13.86	9.81	76.32	4	408
SB8	652	13.50	9.97	76.53	4	434
SB9	648	14.97	8.95	76.08	2.1	356
SB10	646	14.24	9.13	76.63	3.5	396
SB11	643	14.46	10.1	75.43	4	412
Long barrel						
LB1*	653	14.70	9.95	75.34	6.6	492
LB2	644	13.82	9.47	76.71	5.9	468
LB3*	650	14.15	10	75.85	5.5	420
LB4	649	14.33	10.02	75.65	6.6	453
LB7*	661	14.22	9.68	76.10	6.6	427
LB8	652	14.26	9.50	76.22	5.8	449
LB9	653	13.94	9.80	76.1	6.5	470
LB10	650	13.54	10	76.23	6.7	480

+ Al/KIO₄/CuO/PTFE, *Tube failure.**Table 4-14.** Altered slapper elements loading and performance

Test	Total Mass (mg)	G (wt. %)	Al/CuO (wt. %)	Comp ⁺ (wt. %)	Barrel length (mm)	Peak velocity measured (m·s ⁻¹)
Long tube short barrel						
LTSB1	650	13.85	9.85	76.31	4	409
LTSB3*	648	14.04	9.88	76.08	4.5	377
LTSB5	650	14.15	8.92	76.92	3.9	439
Short tube heavy load						
STHV2	658	8.97	9.73	81.30	1.3	342
STHV3	650	9.23	9.23	81.38	3	367
STHV4	653	9.34	9.34	81.32	3.5	362
STHV5	636	10.06	10.06	79.87	4	427

+ Al/KIO₄/CuO/PTFE, *Tube failure.

It was not possible to track the projectile emerging from the barrel due to the flash produced by the reaction. Once the projectile escaped from the obscuring cloud of combustion products it could be tracked as shown in Figure 4-30.

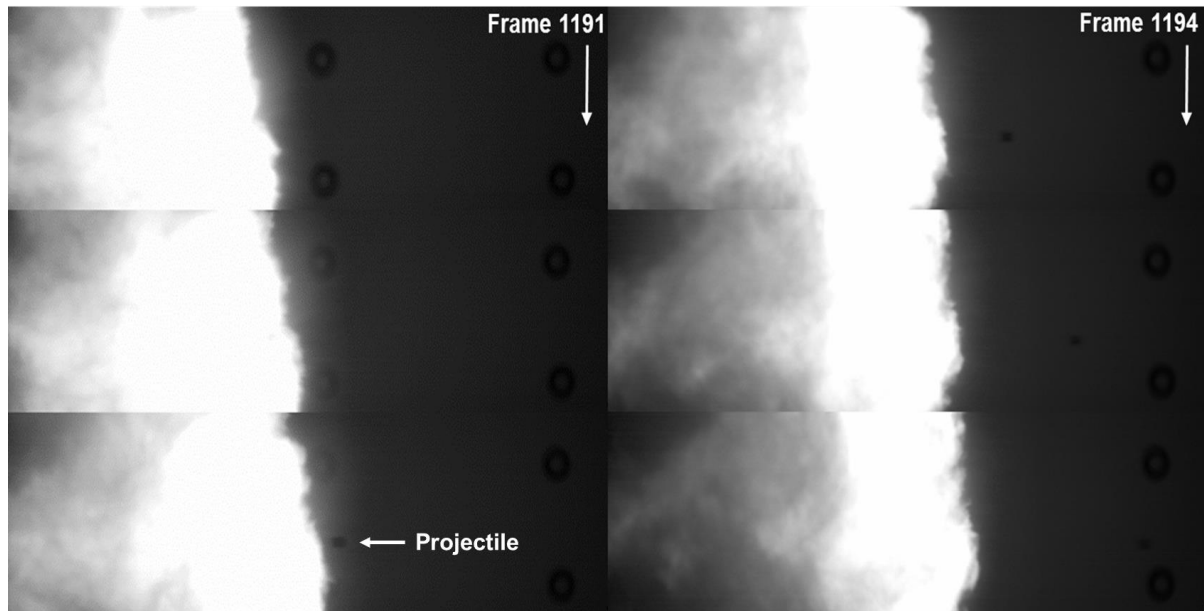


Figure 4-30. High-speed imaging results for SB7.

The average velocity of the projectile was determined over a distance of approximately 100 mm in the horizontal plane. The average velocities recorded for four element types are shown in Figure 4-31.

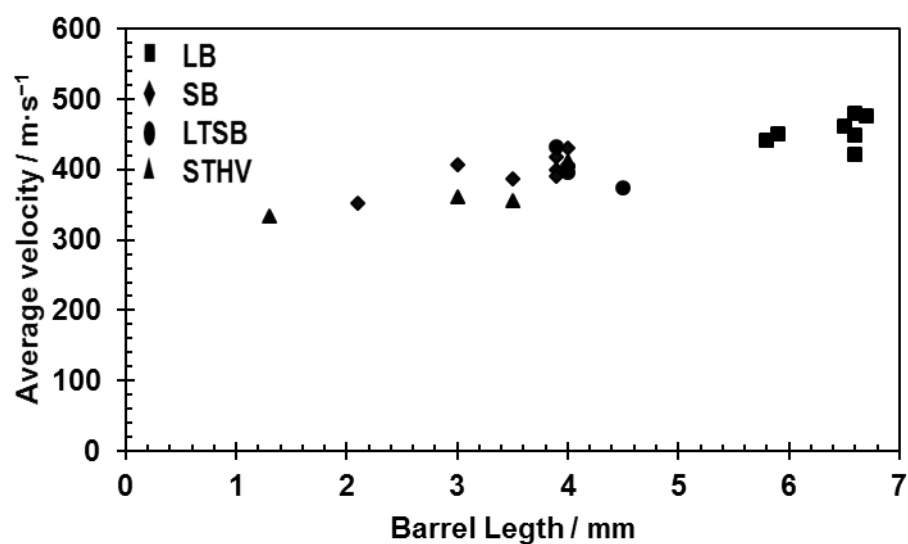


Figure 4-31. Velocity as a function of barrel length for element types.

Mention must be made that numerous element failures occurred during the data collection tests. The LB and LTSB data sets have a few gaps due to tube failures. In some cases data could be obtained but in others the tube failures resulted in a significant distortion of the video image recordings. Examples of these failures are shown in Figure 4-32.

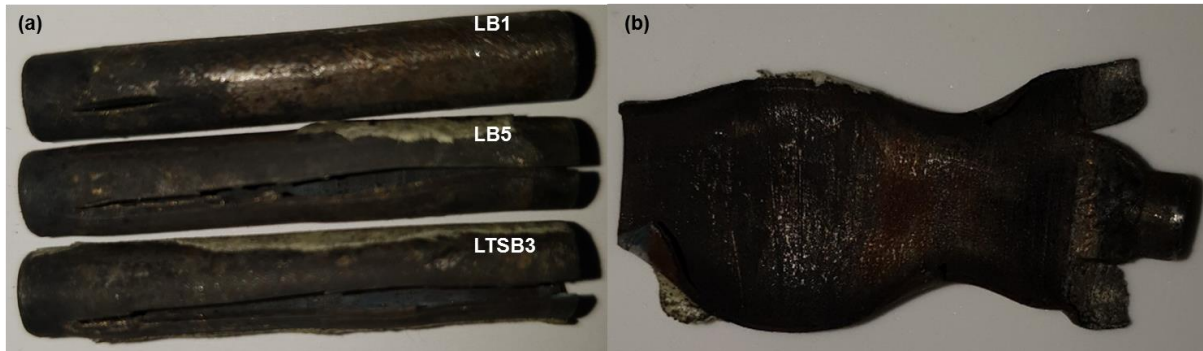


Figure 4-32. Examples of failure in the 29 mm tubes (a) and example of an unsupported element burn (b).

The LTSB sample set had a failure rate of almost fifty percent. A reason for this may be the lower density of the composition within the combustion chamber. It was suggested in earlier chapters that the reaction of this composition follows a convective mechanism. The lower loading density in the larger combustion chamber of the LTSB sample would have allowed faster reaction rates. Tube failure can be explained by the imbalance between the rate at which the combustion chamber pressurises and the rate at which it expands due to projectile motion down the barrel. Unfortunately, the high frequency of the failures as well as the extent of the failures makes it difficult to draw substantive conclusions, e.g. on the effect the velocity of the projectile may have had. What is clear, is that the elements do not survive when fired in an unsupported manner, as is evident from the results in Figure 4-32 (b).

Alteration of the loading procedure, STHV, did not yield any perceivable performance boost compared to the SB. Figure 4-33 shows material traveling down range in the wake of the projectile. This suggests that the projectile left the barrel, before complete combustion occurred.

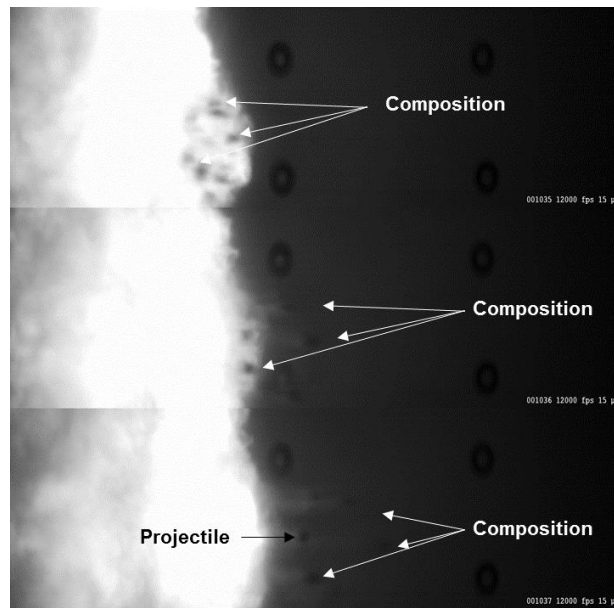


Figure 4-33. Three frames from a SB trial showing media other than the projectile being expelled from the barrel.

The muzzle velocities were estimated for the SB and LB element types. These velocities had to be inferred from calculations due to the obscuration of the projectile when close to the element exit. The model of Allen (2018) was used to fit the experimental data as shown in Figure 4-34.

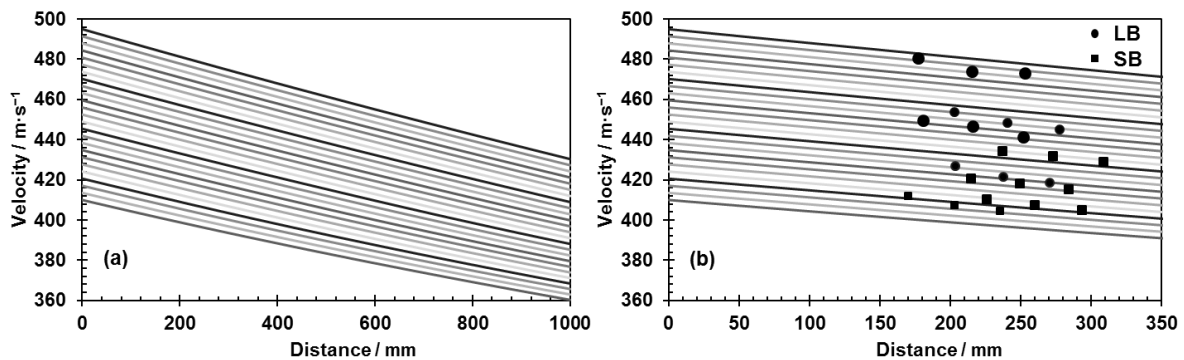


Figure 4-34. (a) Projectile velocity over distance, (b) experimental data fit to calculated velocities.

The measured velocities, obtained with the LB and SB element types, were compared to the predicted velocity profiles. This allowed the estimation of the muzzle velocity achieved for each element type. The average muzzle velocity of the SB type elements was $434 \pm 14 \text{ m} \cdot \text{s}^{-1}$, while the LB was $475 \pm 17 \text{ m} \cdot \text{s}^{-1}$.

The long and short barrels were also fired at aluminium witness blocks to illustrate the impact the projectile can have on a target. The results of these tests are shown in Figure 4-35 and Figure 4-36.

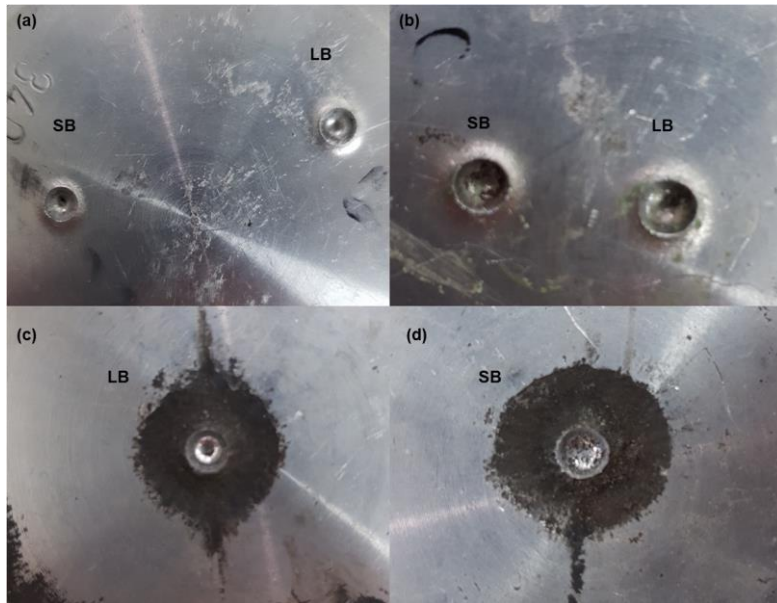


Figure 4-35. Impact demonstration, (a) target at 24 cm from element, (b) target 5 cm from element (c-d) targets in contact with the element.

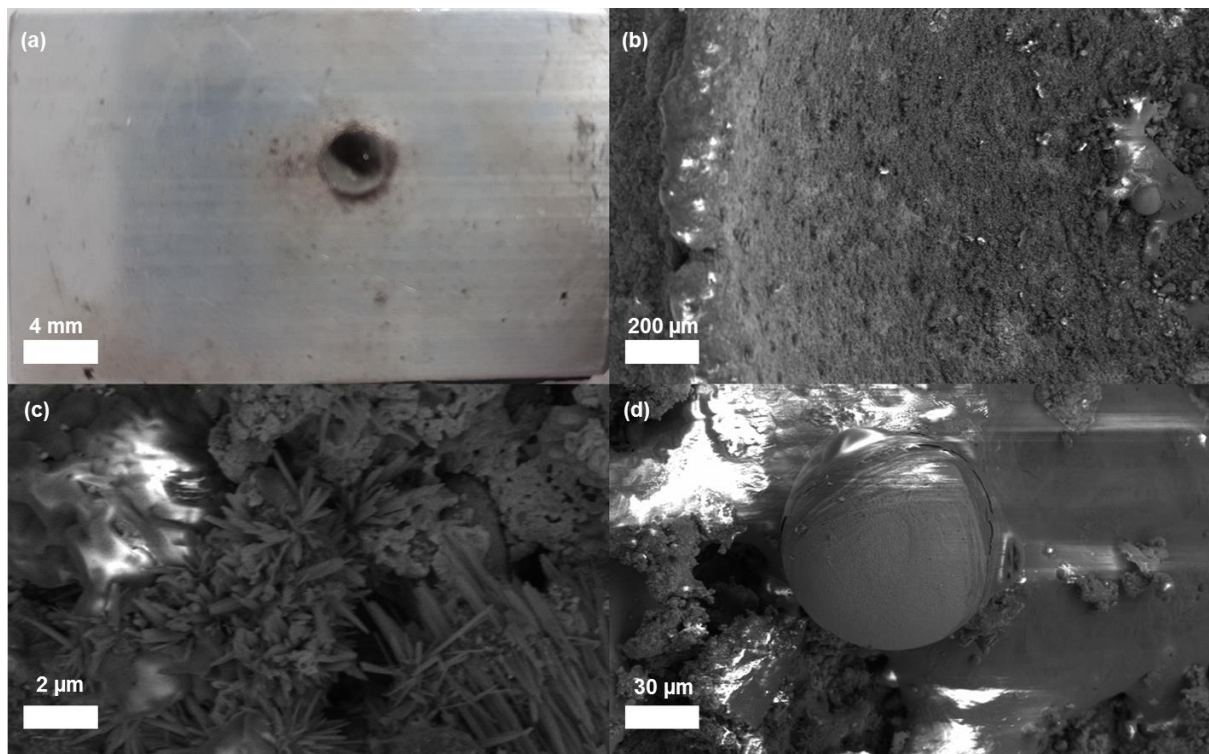


Figure 4-36. SEM imaging of a 3.1 mm thick aluminium target shot by a SB element at 5 cm

The impact craters shown in Figure 4-35 and Figure 4-36 demonstrate the damage that the projectile and muzzle flow can do. The targets placed in direct contact with the elements showed significant thermal damage around the impact crater. EDX analysis confirmed that the surface deposits, evident in Figure 4-36 (b-c), are burn residues originating from the combustion of the composition. The different morphology differences seen in the material most likely stems from slight differences in the composition of the deposited material. The needle-like structures contained lead which derived from the G composition. However, the spherical particles present, proved to be lead-free. The crater dimensions, work done, estimated impact and expected velocity are shown in Table 4-15 and Table 4-16.

Table 4-15. Crater dimensions and impact data

Element	Distance from target (cm)	Width (mm)	Depth (mm)	Work ^a (J)	Work ^b (J)	Kinetic energy estimate (J)
SB	24	3.9	2	15.49	32.28	22.90
SB	5	4.02	2.25	-	38.96	24.15
SB	0	3.75	1.25	10.95	18.43	24.49
LB	24	4.02	2.25	-	38.96	27.42
LB	5	4.05	2.5	-	44.04	28.92
LB	0	3.8	1.6	12.13	24.32	29.33

(a) Area expansion, (b) constant area

Table 4-16. Calculated velocity comparison

Element	Distance from target (cm)	Calculated ^a velocity ($\text{m}\cdot\text{s}^{-1}$)	Calculated ^b velocity ($\text{m}\cdot\text{s}^{-1}$)	Expected velocity ($\text{m}\cdot\text{s}^{-1}$)
SB	24	345.2	498.3	420
SB	5	-	547.4	431
SB	0	290.2	376.5	434
LB	24	-	547.4	459
LB	5	-	582.0	472
LB	0	305.5	432.5	475

(a) Area expansion, (b) constant area

Surprisingly, the impact crater depth caused by the two elements that were in direct contact with the targets were shallower than those that were placed at some distance. There are a number of possible reasons for this. The first is an effective shortening of the barrel due to the fact that the projectile impact occurred even before it has left the barrel. The barrel was

effectively shortened by one projectile diameter. The speed at which it hit the target was therefore somewhat lower. Furthermore, due to the unsupported nature of the target the gasses driven from the barrel by the projectile could dampen the impact by moving the target in the direction of the projectile thereby limiting the impact force.

Since the projectiles are practically identical in mass and dimensions the only variable was the velocity at impact. The difference in velocity explains the results seen for the blocks placed at a distance from the elements. The closer targets had a deeper indentations indicating higher impact velocities. As expected, the longer barrels produced higher velocities. The estimated work done, on the targets placed at 5 cm and 24 cm, exceeded the energy required to initiate PETN by impact, see Table 4-3.

The work energy theorem was used to estimate impact velocities shown in Table 4-16. The velocities differed significantly depending on which equation was used. Equation 3-4 assumes that the indentation diameter remains constant. Equation 3-5 considers the expansion of the indentation as the projectile pushed deeper into the target. This equation is, however, limited to penetration diameters that are smaller than that of the spherical projectile. Further differences are seen when comparing the data to the expected velocity. Due to the simplistic design of the element and slight variations in the loading procedure some variation was expected. Both the model used for determining the muzzle velocity and the velocity of impact are simplified representations of the problem. That said, it is also to be expected the projectile's kinetic energy is not completely converted into deformation work done on the target. This stems from the fact that energy is dissipated into the target and surroundings by a variety of means and because the projectile did not actually come to a halt in the target.

In order to determine the feasibility of the design impact simulations were run with projectile velocities in the range $354 \text{ m}\cdot\text{s}^{-1}$ to $492 \text{ m}\cdot\text{s}^{-1}$. The velocity range was chosen as it encompasses most of the measured velocities as well as the calculated muzzle velocities. The procedure described in Section 2.5.3.3 was used to determine whether the projectile velocity achieved would be sufficient. For the purposes of these calculations the target explosive was chosen to be PETN with a density of $1.6 \text{ g}\cdot\text{cm}^{-3}$ the critical initiation criteria can be found in

Table 2-4 and Figure 2-15. Furthermore, for ease of calculation, the projectile was modelled as a disk with a diameter and thickness equal to that of the bearing. The results of the calculations are shown in Figure 4-37 and Figure 4-38.

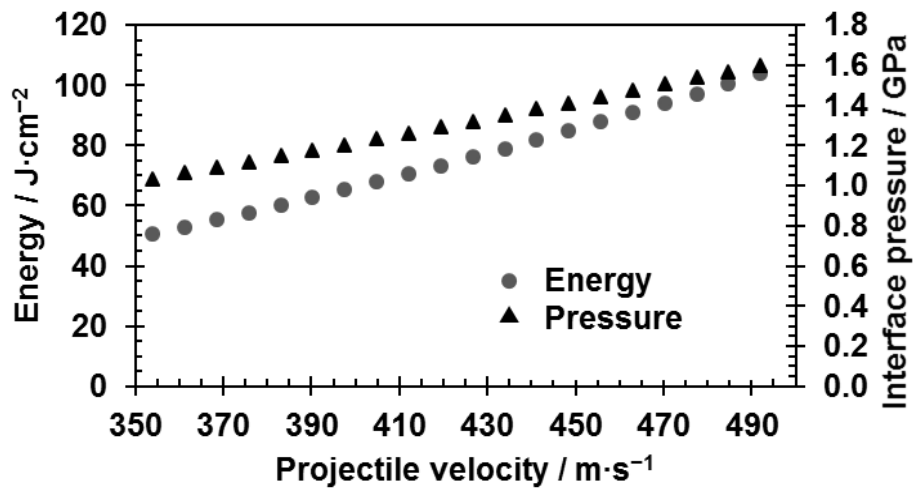


Figure 4-37. Impact energy and interface pressure for projectiles shot from SB and LB elements.

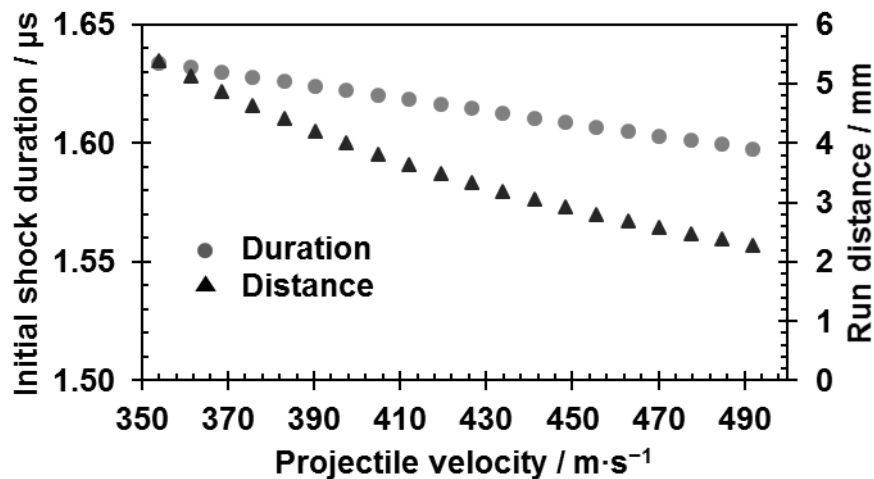


Figure 4-38. Initial shock duration and run distance to detonation for projectiles shot from SB and LB elements.

However, the data in Figure 4-37 do indicate that the impact of the projectile far exceeds the minimum requirements for impact initiation. The run distance in Figure 4-38 is 5.4 mm and 2.29 mm at the extremes. It was mentioned in Section 2.5.3.3 that the pressure pulse should maintain a peak pressure in the explosive for at least the ideal run distance described by the Pop-plot data. Another criterion is that the diameter of the flyer should be at least double the length of the run distance. The first criteria is easily met with the maximum pulse distance being greater than five times that of the Pop-plot results. The second criterion is, however, not met except for the one data point close to 2.29 mm.

The results obtained with the simple delay element modification compares relatively favourable with the Glavier et al. (2017) nano-composite system. They propelled a 40 mg stainless steel disc to speeds ranging from 665 m·s⁻¹ to 1083 m·s⁻¹. In order to achieve these velocities, they used an 8 mm long barrel. The modified delay elements used in these trials lost pressure through the ignition port and did not seal as well as the intricately machined system developed by Glavier et al. (2017). However, the present system illustrates the potential of a purely pyrotechnic composition to perform a similar role. However, further refinement of the concept is indicated.

4.8.4.1 In detonator testing

Due to the confinement issues found in the previous detonator trials, the elements were tested in copper-nickel shells only. Once again, the results indicated that the pressures involved exceeded the capabilities offered by these detonator shells. The loading parameters, as well as the results obtained from long and short barrel burns, are shown in Table 4-17 and in Figure 4-40 to Figure 4-41.

Table 4-17. FPD element loadings for detonators

Test	Total Mass (mg)	G (wt. %)	Al/CuO (wt. %)	Comp ⁺ (wt. %)	Barrel length (mm)	Result
Short barrel						
SB1	643	14.6	10	75.4	5	Fired
SB2	655	14.4	9.1	76.5	4.4	Fired
SB3	646	14.1	9.6	76.3	4.35	Fired
SB4	654	14.7	9.8	75.5	4.65	Fired
Long barrel						
LB1	651	14.3	9.4	76.3	6.6	Fired
LB2	660	14.2	9.1	76.7	5.5	Fired
LB3	638	13.5	9.4	77.1	6.6	Fired

+ Al/KIO₄/CuO/PTFE,

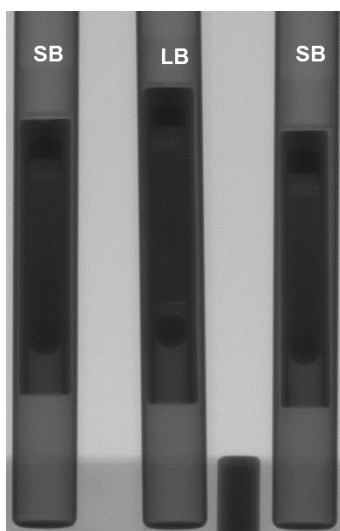


Figure 4-39. X-ray imaging of SB and LB elements in in copper-nickel shells.

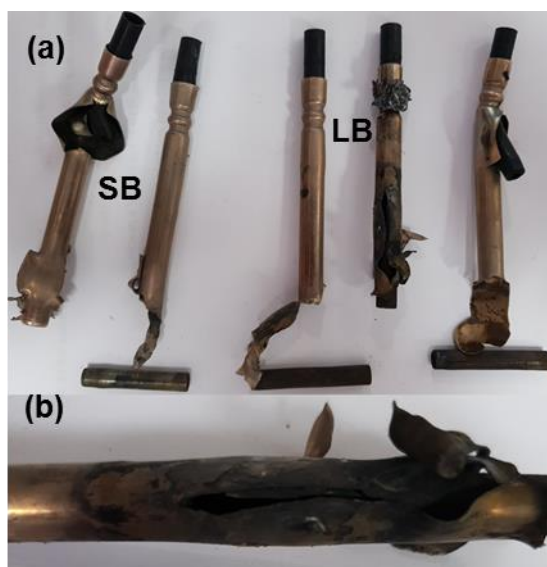


Figure 4-40. (a) Copper-nickel shells containing long and short barrels post burn. (b) Example of element and subsequent shell failure.

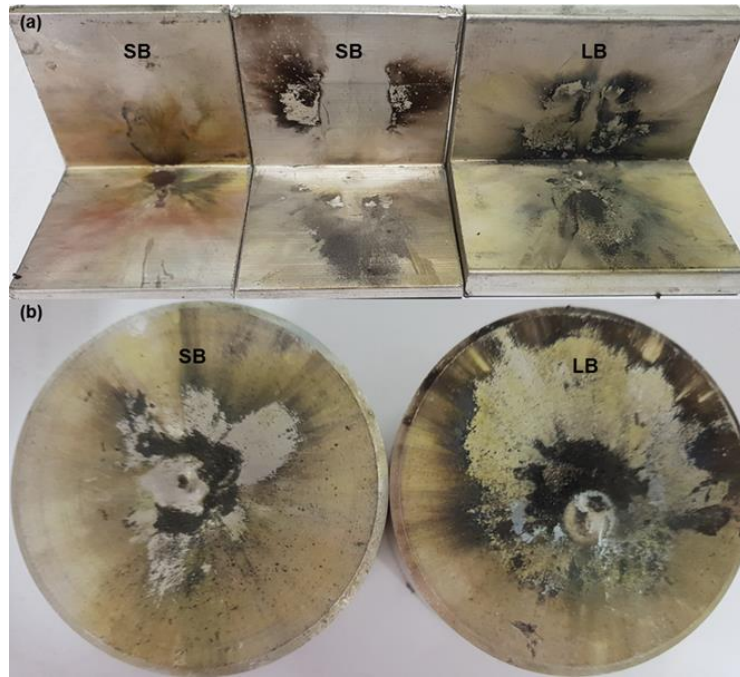


Figure 4-41. Witness plates (a) and blocks (b) for long and short barrels.

Figure 4-39 shows the two element types loaded into the detonator shells. In the case of the LB element a gap can be seen between the bearing and the composition. Unfortunately in these images the PETN is transparent which makes it difficult to tell whether some of the PETN base charge moved into the barrel cavity.

Figure 4-40 shows the problems experienced with confinement. In some instances, the shells failed at multiple locations. In one detonator, the long barrel element failed causing a tear in the detonator shell, Figure 4-40 (b). The witness plates and blocks shown in Figure 4-41 show some denting and damage similar to that caused by the muzzle flow shown in Figure 4-35 (c) and (d). The thermal damage was less than reported in Figure 4-35 which is most likely due to the indirect nature of its application due to intervening materials. The thermal damage, indentation and impact damage are shown in Figure 4-42.

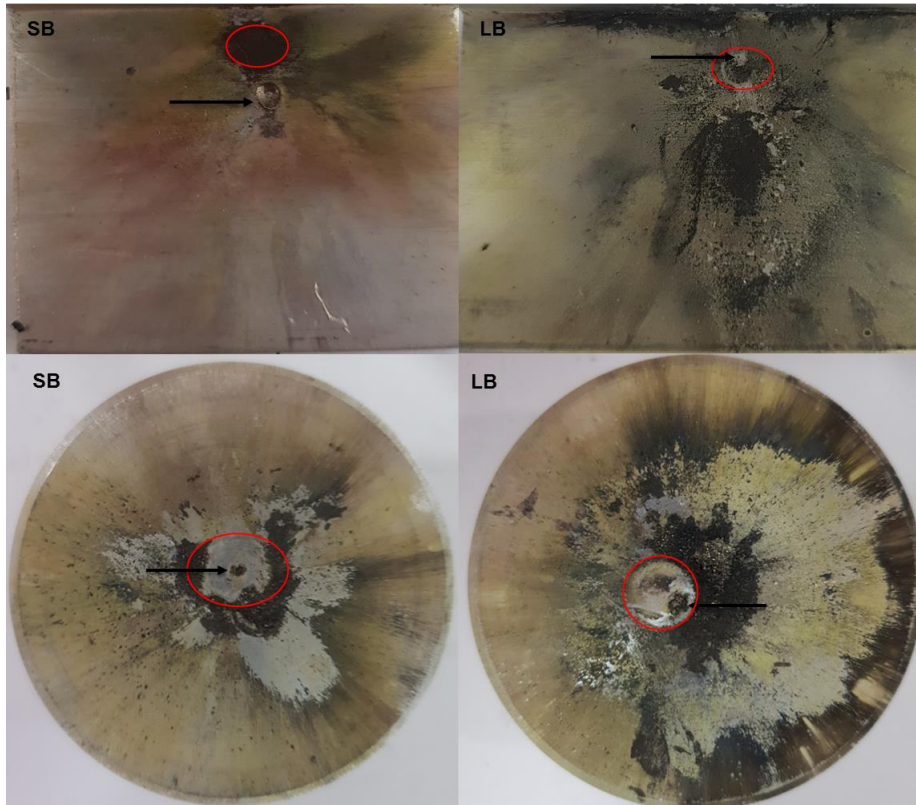


Figure 4-42. Witness blocks and plates for SB and LB element types. Circled area indicates indentation. Arrows indicate potential bearing impact.

4.8.5 Ballistic model and improvements

At this stage no clear evidence for initiation was recorded, some suggestions as to why this has occurred has been discussed preceding text. A simple model was set up to determine the possibilities for improving the design of the element. By modelling the element in a manner similar to the gas gun example in Chapter 2.5.3 the problem could be split into two parts. The first being the combustion chamber and its pressurisation. Followed by the projectile motion down the barrel.

4.8.5.1 Projectile motion

Since the exact moment of projectile release is unknown, a preliminary check was run on the pressurisation model. This was to see if the pressure generated within the combustion chamber exceeded that used to force the projectile down the barrel. This system was just another iteration of the gas gun model discussed in Section 2.5.3. For simplicity it was assumed that the projectile only starts its acceleration once the chamber is “fully” pressurised. It was also assumed that all the work done by the gas was directly converted into the kinetic energy of the projectile, 4-1 (Carlucci and Jacobson, 2008). The barrel diameter was constant so the gas volume is defined by the position of the projectile within the barrel, Equation 4-2 .

Since the process is isentropic, the gas temperature change according to Equation 2-79 as modified using Equation 4-2 to give 4-3.

$$KE = \frac{1}{2}mv^2 = w = \int PdV \quad 4-1$$

$$V = A \times l \quad 4-2$$

$$T = T_i \left(\frac{l_c}{l} \right)^{(\gamma-1)} \quad 4-3$$

Combining Equations 4-1 to 4-3 with the ideal gas law results in Equation 4-4.

$$w = nRT_i l^{(\gamma-1)} \int_0^{L_m} (l+x)^{-\gamma} dx \quad 4-4$$

It links the work done on the projectile to its relative position in the barrel; where (l) represents the chamber length and (x) represents the distance of the projectile base into the barrel. The projectile has left the barrel when the base distance from the barrel chamber interface equals L_m . The initial gas temperature (T_i) must be known along with the number of moles of gas.

Integration of Equation 4-4, equating it to the kinetic energy of Equation 4-1 yields Equation 4-5 after some rearrangement.

$$v = \sqrt{\frac{2nRT_i l^{(\gamma-1)}}{m(1-\gamma)} [(l+L_m)^{(1-\gamma)} - l^{(1-\gamma)}]} \quad 4-5$$

Therefore, the muzzle velocity can be estimated by knowing only the initial gas amount, the barrel and chamber lengths, the initial temperature and the projectile mass (m).

The open burn combustion temperature reported earlier was taken as the initial temperature for the combustion chamber. At this temperature, not all of the combustion products are expected to be in the gas phase. However, for ease of calculation, complete conversion of the composition to gas was assumed.

4.8.5.2 Model results

Average chamber length and compositional mass varied slightly between the two element types. It was accounted for when setting up the model to compare with the experimental muzzle velocities. The simulated velocity of the projectile, as it proceeds down the barrel, is shown in Figure 4-43. The projectile is superimposed on the graph to illustrate that, for these

simulations, the barrel length included the space occupied by the projectile. However, the previously reported barrel lengths did not include it.

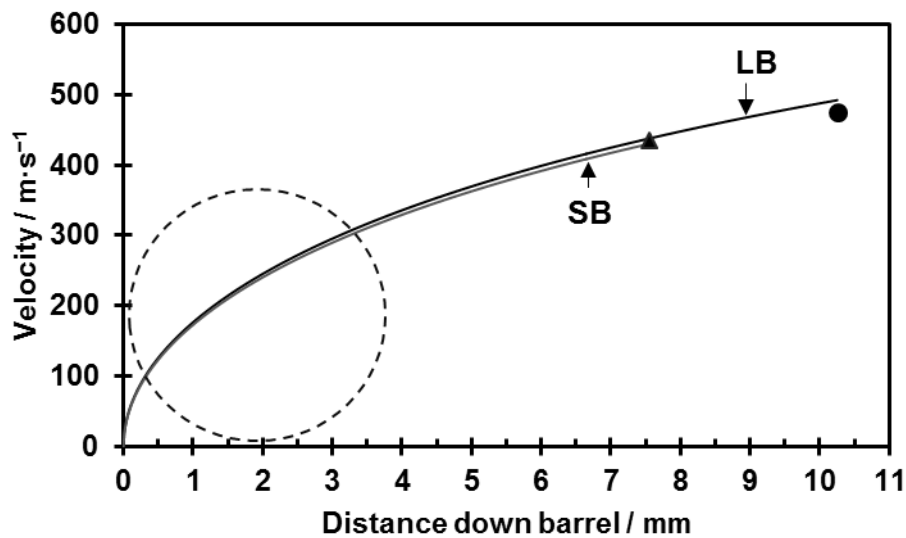


Figure 4-43. Down barrel velocity for LB and SB element types. (▲) Average measured muzzle velocity of SB elements. (●) Average muzzle velocity of LB elements. The initial temperature of the chamber was set at 2091 K.

Figure 4-43 indicates that the simple model fits the experimental results well. The simulations shown in Figure 4-44 to Figure 4-46 varied the barrel length, projectile mass and composition loading. All of these simulations were based of the initial loading procedures or dimensions of the LB elements with an initial chamber temperature of 2091 K.

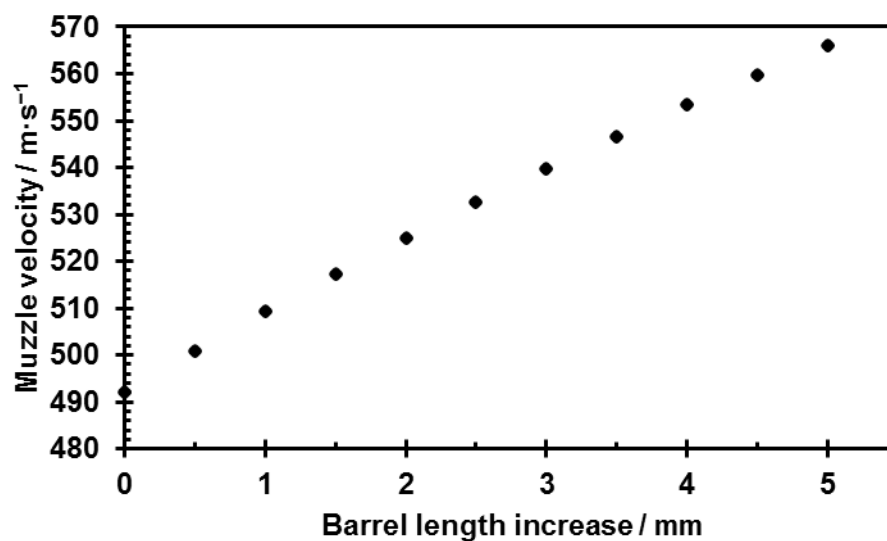


Figure 4-44. Effect of barrel length on muzzle velocity.

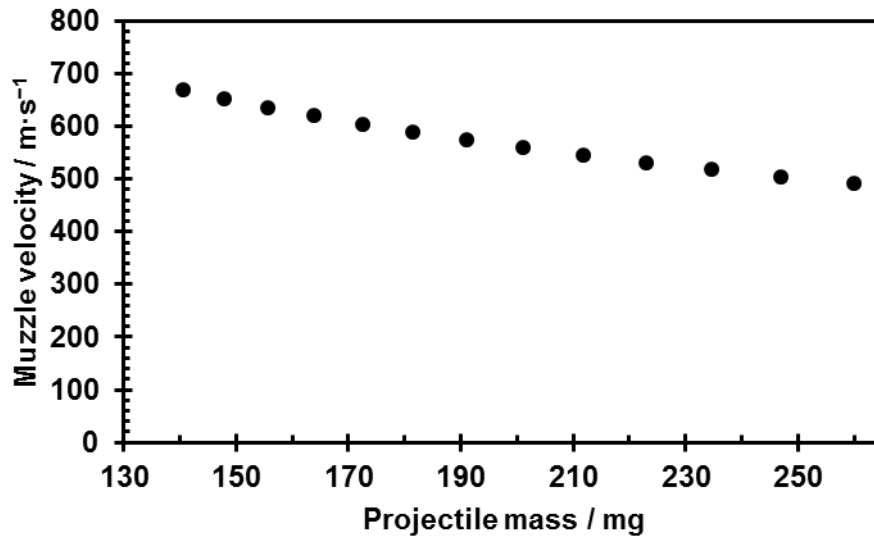


Figure 4-45. Impact of projectile mass on the muzzle velocity of the LB elements.

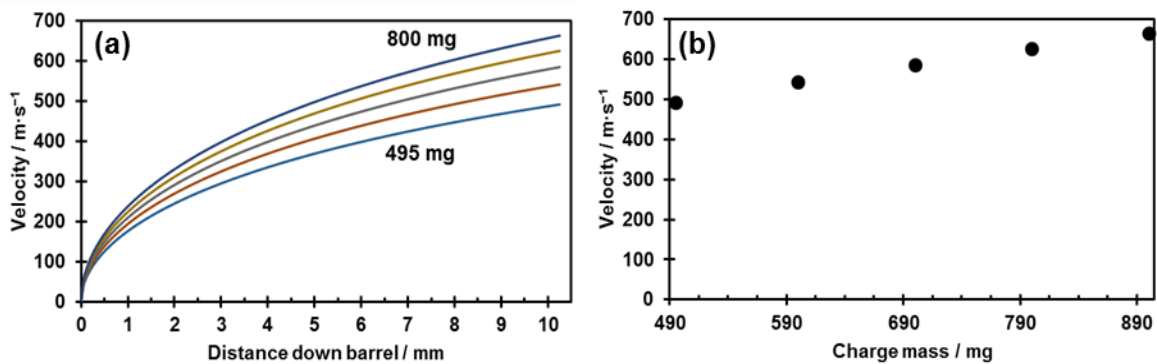


Figure 4-46. (a) Projectile velocity variation with charge mass. (b) Muzzle velocity variation with charge mass.

As expected, a longer barrel results in a higher muzzle velocity. However, this affects the space available for the base charge within the detonator. A 5 mm increase in element length leads to a 20 % increase in the muzzle velocity. Alternatively, a reduction in the projectile mass by 50 % leads to approximately 40 % increase in the muzzle velocity. In Figure 4-46 the composition loading was increased. This should lead to an increase in muzzle velocity as seen in the Figure. However, without changing the dimensions of the element, the density of the composition within the combustion chamber will be increased. This in turn will change the combustion properties of the composition which means that the results shown in the Figure may be considerably off. It was also seen that heavier loading led to more tube failures. For this reason, the discussion will be limited to the possibility of extending the barrel and/or lowering the projectile mass.

Increasing the barrel length is possible but is associated with the same problem of changing the dimensions of the element. The next problem that may arise is tube failure due to the time the projectile spends in the barrel. Unlike this simple model where the initial chamber pressure is not an issue, in the real system the pressure can exceed the mechanical limits of the containment used. The pressure rise is counteracted by the motion of the projectile down the barrel. Higher pressures should lead to higher projectile velocities, see Equations 2-73, 2-74 and 2-75 finding the balance is the problem. The compositional loading should be such that the maximum pressure from the start of ignition to the point at which the projectile leaves the barrel should not exceed what the system can contain. Therefore, the simplest solution would be to reduce the projectile mass.

5 Discussion

5.1 Mixing methods

Due to the complex nature of the multicomponent systems investigated, only stoichiometric mixtures were used over the course of the investigation. Dry mixing the aluminium with the potassium periodate was found to be inefficient since ignition was difficult if not impossible to achieve. Particle size reduction of the potassium periodate by means of milling did not alleviate the problem. These ignition difficulties were expected since similar difficulties have even been reported for nano-based compositions.

Changing the mixing method to the recrystallization method improved the ignitibility of the composition when the appropriate starter composition was used. The improved ignitibility of the composition is most likely due to the enhanced contact between the particles. Microscopy confirmed agglomerates of aluminium and potassium periodate crystals.

It is possible that wet mixing might have slightly reduced the fuel content of the aluminium. However, an iodine test indicated that in the timeframe of the mixing procedure used there was little to no interaction between the aluminium and dissolved potassium periodate. This does not rule out the reaction between the aluminium and water. This means that further testing is required should the mixing process be scaled up to larger quantities, e.g. as in industrial spray drying. This is because a reaction between aluminium and water will produce hydrogen gas which is an explosion risk.

5.2 Ignitibility, heat of reaction and sensitivity

The base composition, consisting of just aluminium and potassium periodate, did not feature a thermal runaway in the DTA. The conditions within the DTA did not provide the composition with the ideal conditions to initiate ignition. This is due to the inert atmosphere and small sample mass, as well as the instrumental limitations on the heating rate. A faster heating rate and/or running in an oxygen atmosphere should enhance the ignitibility, but would provide little information regarding the ignition mechanism likely to be in action during actual applications.

In order to improve the ignitibility of the base aluminium potassium periodate composition blending was considered. A number of additional compositions were explored. The intent was altering or outright changing the ignition mechanism. The additive compositions used were stoichiometric mixtures of Al/CuO, Al/PTFE, Al/S and S/KIO₄. The base composition was theorised to react in a gas-solid manner. This is because the decomposition of the oxidiser to

gaseous components occur at temperatures significantly lower than those at which the aluminium becomes receptive or reactive due to the phase changes of its native oxide layer. The additives were chosen with the intent to act at different stages of the heating cycle with the purpose of finding a system capable of thermal runaway.

Sulfur has a low ignition temperature suggesting that it could facilitate the ignition of the bulk composition. Fluorine-containing species from decomposing PTFE can react with alumina to expose the underlying aluminium. Copper(II) oxide is a stable oxidant that only becomes reactive at high temperatures closer to that at which aluminium is in a more reactive state.

The addition of sulfur containing compositions looked promising. The combination of sulfur and potassium periodate would have a strong exothermic response below the decomposition temperature of the potassium periodate. Its addition to the base system showed promise but did not lead to complete combustion of the aluminium. Instead the thermal response indicated an initial sulfur reaction with the potassium periodate followed much later by aluminium oxidation. Thermal runaway was achieved with the addition of PTFE. The thermal runaway event initiated in the region of 490 °C for S/KIO₄ containing system. For the Al/S system it was about 505 °C. The sulfur-containing systems were very sensitive to the overall sulfur content showing an inverse response when adding S/KIO₄ or Al/S.

Combinations of the Al/KIO₄ composition with the Al/CuO composition did not result in a thermal runaway event. The same was not true for the combination with the Al/PTFE composition. Thermal runaway was achieved for the composition containing PTFE. Depending on the PTFE content, the event was initiated between 480 °C and 510 °C.

The addition of Al/CuO and Al/PTFE compositions to the base composition reduced the ignition temperature of the composition to between 470 °C and 480 °C. This is approximately a 150 °C decrease from the expected ignition temperature. The reason for the drastic decrease witnessed is thought to be due to a change in mechanism brought on by the addition of PTFE. It is theorised that this occurs by means of a pre-ignition reaction between the aluminium oxide, PTFE decomposition products and potassium periodate decomposition products. The decomposition of the potassium periodate and PTFE is enhanced by a catalytic interaction with copper(II) oxide within the composition further enhancing the process. Due to the slightly lower ignition temperature and lower sensitivity to minor composition changes the copper(II) oxide and PTFE additives were chosen for the subsequent trials. The sensitised compositions were mixed in the following mass ratios [Al/KIO₄]:[Al/CuO] 90:10 and [Al/KIO₄]:[Al/CuO]:[Al/PTFE] 90:10:5.

Combustion product analysis for the base composition and the two sensitised compositions illustrated the complexity of the system. The initial expectation was that the aluminium would be fully oxidised and the oxidisers would be completely reduced. This appeared to be the case for Al/KIO₄ composition as the only solid combustion products recovered were alumina and potassium iodide. The Al/KIO₄/CuO composition produced unexpected products. Firstly aluminium reacted with potassium and oxygen to form potassium aluminate. The copper recovered in the burn residue was located in the copper(I) iodide compound. The Al/KIO₄/CuO/PTFE composition complicated the situation even further by forming copper(II) iodate. This particular result is interesting as there was no evidence of the oxidisers reacting when DTA analysis was performed on mixtures of the oxidisers, see Figure 4-9. This implies that the reaction of the potassium periodate is not with the copper(II) oxide but rather with the copper formed from its reduction by aluminium.

One also needs to consider the possibility of alternative reaction routes being possible under bomb calorimeter conditions. The DTA results were obtained at atmospheric pressure whereas the bomb calorimeter had a starting pressure of 3 MPa which would rise further with the production of gaseous species and the rise in temperature. At these pressures components that were not in a state to readily interact under atmospheric conditions may well be in contact allowing for alternative interactions to take place. It is clear at this point that the reaction mechanism is not yet fully understood. Investigating the oxidiser decomposition mechanisms and interactions under different environments can provide insight into the intermediate compounds that form.

Improving the ignitibility of the base composition is not without its drawbacks. A number of properties changed with the inclusion of the additive systems. This is expected as an increase in components within the system increases the complexity of the mixing process. In order to obtain reliable combustion performance, the proper distribution of the components within the composition has to be achieved. Due to the differing densities and particle sizes of the components used operating at low densities can cause the compositional distribution of the composition to change due vibration induced separation.

This increase in complexity and potential component distribution gradients is thought to be a reason for the increase in variance seen in the calorimetry data, Table 4-6. The addition of the other two thermites had a minimal effect on the energy output of the base composition. Slight increases were documented with the addition of the sensitising compositions but due to the variance there is overlap of the runs indicating that the effect may be minimal or that there are slight compositional differences within the bulk material which slightly skews the data.

The additional components blended with the base composition also altered its sensitivity to other forms of initiation. Impact sensitivity remained almost unchanged while the friction sensitivity decreased and the sensitivity to electrostatic discharge increased. The changes in sensitivity are due to the way in which the different components interact with these stimuli. PTFE has a lubricating effect which could explain the 72 N decrease in sensitivity when compared to the base composition. The increase in sensitivity toward ESD is thought to be due to the inclusion of copper(II) oxide as it has been reported to be more sensitive than mixtures between aluminium and PTFE to this particular stimulus.

The base composition as well as the sensitised composition compare favourably when compared to the primary explosives listed in Table 4-3. This is ideal as the intended purpose for the composition is to work with if not outright replace these compounds in chemical delay detonators. In any case, it is beneficial from a safety aspect to be less sensitive to unwanted initiation.

5.3 Combustion performance

The Al/KIO₄ composition showed a drastic increase in burn rate when the change was made to enclosed burns. This indicates a strong reliance on convective heat transfer to drive the reaction front. In the case of pure conductive heat transfer confinement would not be expected to play such a big role as system pressure would have a smaller impact on the overall burn rate. This was seen in the case of the aluminium and copper(II) oxide composition which had a comparatively small increase in burn rate from the open to enclosed burns.

Both the Al/KIO₄/CuO and Al/KIO₄/CuO/PTFE compositions performed better than the Al/KIO₄ compositions in these trials. The same pressure driven improvement in the burn rate was expected as for the base composition. The addition of the additives provided alternative reaction pathways. Even when accounting for the lower combustion temperatures of the additive systems, the overall effect on the sensitised systems was positive from a burn rate perspective. In the case of Al/KIO₄/CuO, the improved burn rate was attributed to a catalytic effect of the copper(II) oxide on the decomposition of the potassium periodate. Furthermore, the formation of copper(I) iodide, found in the combustion product analysis, contributed to gas formation. This is because copper(I) iodide has a lower boiling point than metallic copper. It is also significantly lower than that of the recorded combustion temperature of the base composition. The presence of more gaseous components is believed to be the driving force behind the enhanced burn rates witnessed.

The faster combustion rate of the Al/KIO₄/CuO/PTFE composition is thought to be partially due to its lower ignition temperature. It allows for a shorter heating delay before the adjacent region ignites. The shortened ignition delay paired with more gaseous intermediates and combustion products increases the rate of pressurisation under the confined conditions. The combustion product analysis performed on samples recovered from the bomb calorimeter showed an even more complex product distribution with more species available that would be in a gaseous state at the reaction temperature.

The measured velocities indicate that the experimental setup may have limited the maximum burn rates achievable. Evidence for this stems from the fact that two blends Al/KIO₄/CuO and Al/KIO₄/CuO/PTFE had a similar peak velocity approaching 1 km·s⁻¹, even though the former was 150 m·s⁻¹ slower during the first stage of the burn. This indicates that the Al/KIO₄/CuO composition caught up with the Al/KIO₄/CuO/PTFE composition during the second half of the burn. A possibility is that the flame front Al/KIO₄/CuO/PTFE decelerated due to compaction of the unburnt composition ahead of the reaction zone brought on by the increased in pressure. Compositions that burn in a predominantly convective manner perform better at lower densities as there are more pathways for the combustion gasses to exploit and accelerate the reaction. Another explanation for the convergence of the burn rates is the failure of the silica tubes. A burst tube would reduce the maximum pressure within the tube by providing an outlet for the gaseous species generated during the combustion event. This would explain the tendency for the Al/KIO₄/CuO/PTFE composition to be significantly faster during the first half of the burn while seemingly slowing down when compared to the Al/KIO₄/CuO composition in the second half of the burn. The mechanical integrity of the components limited the pressures attainable during a burn which in turn would limit the maximum achievable burn rate.

Very fast burn rates were measured despite the fact that compositions utilised micron-sized components. They compare favourably with rates measured for nano-sized components as shown in Table 2-5. Certainly, it can be concluded that the sensitised composition displayed performance that is traditionally only reported for nano-scale thermites.

Due to the pressure reliance of the composition, these burn rates are not achievable within the confines of the current standard detonator shell. The delay elements used in the present trials ranged from 25 mm to 29 mm in length. These elements are almost four times shorter than the test setup used for burn rate measurements. The expected burn rate and thereby pressure pulse was expected to be too low for direct initiation of a secondary. However it has been shown that high energy gas has the ability to initiate a high explosive charge under the right conditions. The gas produced during the combustion of the thermite may be able to

initiate an adjacent explosive column given sufficient confinement and loosely packed explosive. In such an instance it would be feasible for several ignition sites to form that could lead to a runaway reaction, possibly triggering a detonation.

5.4 Detonator trials

The direct replacement of primary explosives with pyrotechnic alternatives is a challenge. Despite the enhanced combustion performance of the present thermite, it still reacted significantly slower than a primary explosive like lead azide. Ershov et al. (2013) showed that high temperature gasses are able to initiate detonation of PETN. This was the concept that inspired the current investigation into detonator applications. An attempt was made to replicate this effect with the Al/KIO₄/Al/CuO/Al/PTFE composition loaded into the 25 mm elements used in chemical delay detonators. The idea was to direct the combustion gasses towards the PETN. The hope was that igniting the PETN in this manner would result in a transition to detonation.

Direct initiation of a detonation event in the PETN charge proved to be near impossible. The composition produced sufficient heat to ignite the PETN. The nature of the detonator shell failures indicated that the pressure developed within the system was a problem. The aluminium and copper shells tended to fail prematurely. In most instances the shell split close to the interface between the delay element and the PETN base charge. The aluminium elements, used to house the composition, was another source of failure. They tended to rupture during the burns contributing to the fragmentation of the detonator shells seen in Figure 4-27. The shell remains showed evidence of molten and charred PETN. In a few cases no PETN was found due the extent of fragmentation of the detonator shell. This could indicate that in some instances a detonation was initiated. However, no conclusive evidence for a transition to detonation was observed. The results at this stage varied too much to justify further tests with the same materials.

Unfortunately, direct initiation of PETN by the composition failed to materialise. The reason for this was alluded to earlier when discussing the burn rate of the composition. Even though the composition has the potential to burn at extremely fast rates, it needs confinement to achieve these rates. Unlike the primary explosives currently employed, the output of the composition is not instantaneous. This means that the element and detonator shell is exposed to the pressures for a longer time period. If the composition's combustion exceeds the mechanical limits of the detonator then the PETN will not undergo a DDT event. This is due to premature failure and the loss of the pressure required for the transition to DDT. It is for this reason that

DDT devices seen in literature or patents tend to have a reinforced transition region, for example, a sleeve which provides mechanical support to the detonator shell.

Another approach was taken in view of the mechanical failures witnessed. Realising the limitations and potential of the composition, inspiration was sought from FPD type detonators and the composite systems discussed in Sections 2.5 and 2.8. The intention was to contain the combustion gasses within an element with a mechanically sound structure. The intention was to release the energy in a more directed manner. A simple design was chosen for ease of manufacture. The design employed a steel element which was 2 mm to 4 mm longer than the original aluminium elements used. In order to contain the initial pressure build-up, the element was plugged with a steel ball bearing. The results from these tests indicated that mild steel provided insufficient confinement. The shorter barrels, 27 mm elements, with higher composition densities proved to be more reliable. The longer barrels, 29 mm elements, produced higher velocities at the risk of rupturing the element ($475 \pm 17 \text{ m}\cdot\text{s}^{-1}$ compared to $434 \pm 14 \text{ m}\cdot\text{s}^{-1}$). These velocities compare favourably with those reported by Lopez-Pulliam et al. (2020). However, their projectile achieved kinetic energies about an order of magnitude greater than what was achieved presently.

Unfortunately, the longer barrels burst prematurely generating results similar to those discussed earlier. Initial detonator testing with the improvised elements were met with failure. Similar failures occurred as were seen with the standard aluminium elements. As before there was a tendency for the shells to burst. Witness blocks indicated increased damage compared to the standard aluminium elements. However, a full-scale detonation of the PETN base charge did not occur. This is attributed to the premature failure of the detonator shell itself.

Mechanical integrity of the design aside, the system did show the potential for its development into a primary explosive-free initiator. The design can be further optimised by determining the ideal compositional load for the element that would balance maximum muzzle velocity with element survival. It was found that modelling the system as an ideal gas gun tracked the measured muzzle velocities well. Modifying the input to this model showed that the simplest way to drastically increase the muzzle velocity of the element would be to reduce the projectile mass. This could potentially lead to Initiation within a reasonable distance for a pressed PETN charge.

6 Conclusions and recommendations

The intent of the present investigation was to identify a micron-sized pyrotechnic with the potential to initiate a high explosive charge. Such a composition could function as a replacement for the primary explosive charge used in chemical delay detonators. Due to the large-scale production and usage of these detonators the composition in question should ideally be implementable in a manner that does not require the redesign of the detonator itself or drastic retooling of the of the assembly lines.

Towards this end, the Al/KIO₄ composition was selected due its gas generating potential. The ignition difficulties reported for the composition were overcome with the addition of PTFE, further improvements were obtained by the addition of copper(II) oxide. These additions allowed thermal run-away to occur in a less than ideal environments. They resulted in a drastic increase in the enclosed burn rate performance of the composition, without drastically altering its sensitivity to other forms of initiation.

At this point all compositions investigated consisted of stoichiometric blends of aluminium with alternative oxidisers. It is possible that the combustion performance of the composition can be tailored to better fit the intended goal by altering either the ratios used within the Al/KIO₄/CuO/PTFE blend or by altering the compositions of the individual compositions used in the blend. Alternatively, changing the particle size or morphology of the individual components can also alter the combustion performance and sensitivity to various stimuli. Changes in the combustion performance alter the pressurisation rate due to a change in the rate at which intermediate and product species are produced. Stoichiometry changes can also increase or decrease the gas generating potential of the system. Optimising the stoichiometry of the blends and morphology of the individual components fell outside of the scope of the investigation due to the time-consuming nature of such an investigation. However, alternative blending procedures ratios should also be investigated, in particular to adapt the concept for manufacturing via spray drying. This process has specific requirements with respect to particle sizes and morphologies.

In its current state the Al/KIO₄/CuO/PTFE composition has an ignition temperature and a burn rate approaching those reported exclusively for nano-sized compositions. It was demonstrated that these ignition and combustion performance enhancements are most likely due to a change in the ignition mechanism from a gas-solid mechanism, to a more complex mechanism. It entails a gas phase reaction between decomposition products and a gas-solid mechanism responsible for the removal of the alumina coating on the fuel particles. The

removal of this alumina layer facilitates the interaction of bare aluminium with the potassium iodate still present in a condensed form.

An attempt was made to initiate an accelerated DDT reaction in PETN. This was tried because it would require limited to no alteration to the present detonator structure. Unfortunately, this somewhat direct replacement methodology, was not successful. The origin of the problem lies in the vast difference between the reaction rates and thereby the pressurisation rates of thermites when compared to primary explosives. Furthermore, the pressure rise within the detonators exceeded the limits of the materials used. The inevitable shell ruptures caused a loss in pressure which quenched the reactions. Detonation events were not initiated as this prevented the acceleration of the burn front to the point required for the transition to a detonation. It is postulated that the present system will be able to initiate DDT provided the mechanical integrity problem can be solved.

A more drastic detonator design alteration was also considered. It was based on an improvised FPD-style detonator. Two designs were developed featuring different barrel lengths. Both achieved muzzle velocities sufficient, in theory, for the initiation of PETN. Based on these encouraging results they were assembled in live detonator shells. Unfortunately, these modified delay elements did not live up to the expectations in practice. It is believed that premature failure of the shells, with the concomitant loss of pressurisation, prevented the transition to a detonation.

Nevertheless, it was shown that micron-sized compositions, such as Al/KIO₄/Al/CuO/Al/PTFE, do have potential for use in chemical delay detonators. Further adaptation and refinements could even make them viable as replacements for primary explosives. The advantage of such compositions is their greater stability compared to the primary explosives to be replaced.

7 References

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Appendix A: XRD and XRF results

XRD results for the components used in the trials are shown in Figure 1 to Figure 7.

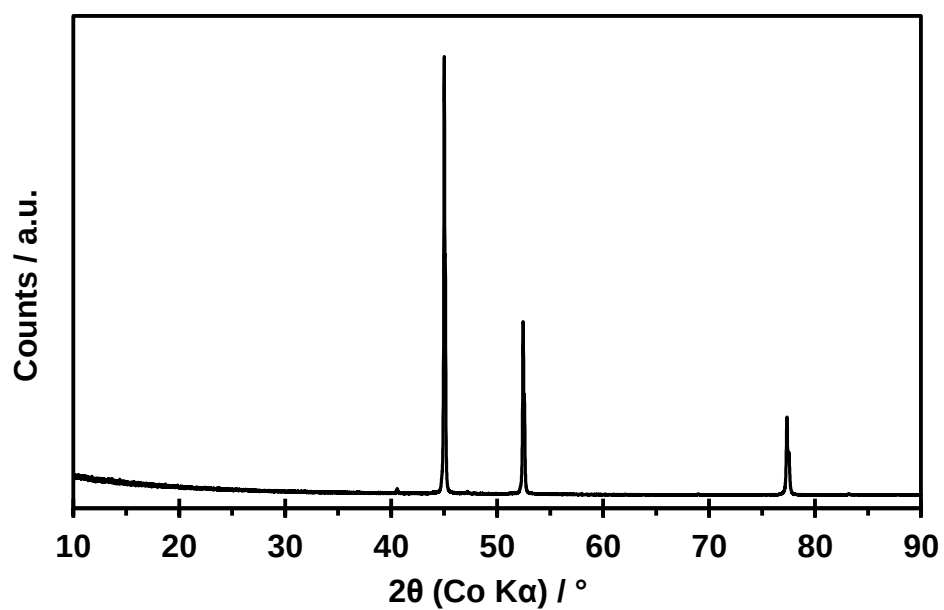


Figure 1. Diffractogram for aluminium.

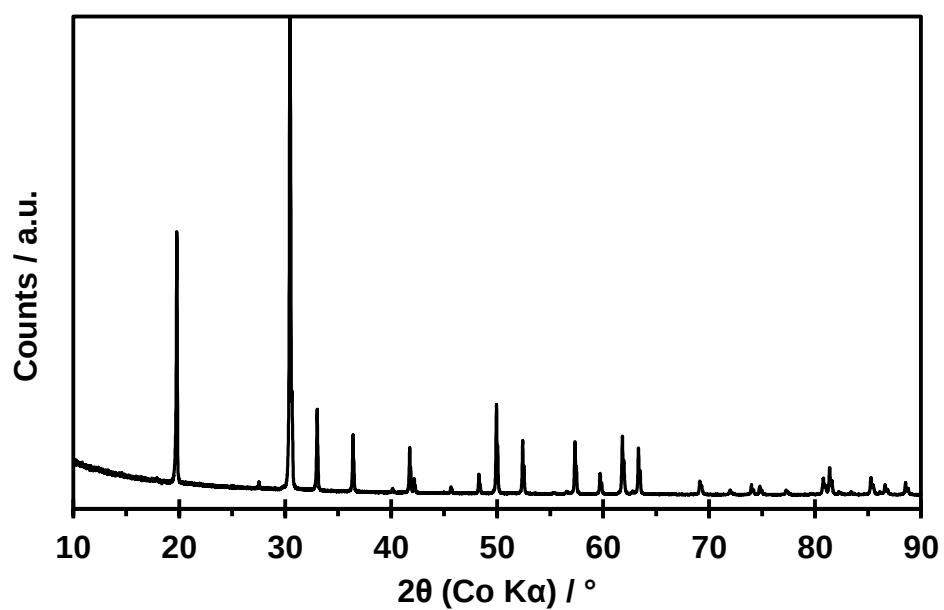


Figure 2. Diffractogram for potassium periodate.

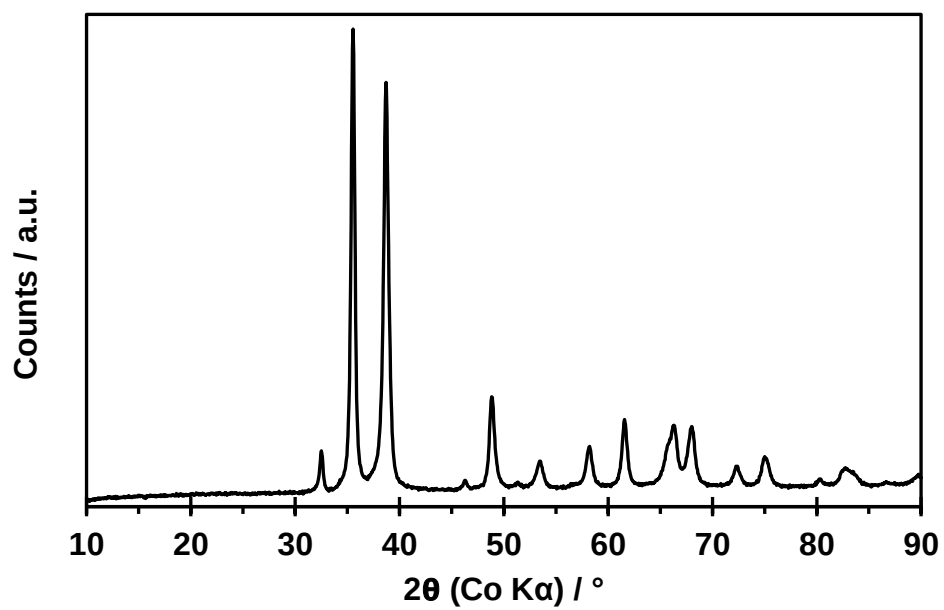


Figure 3. Diffractogram for copper(II) oxide.

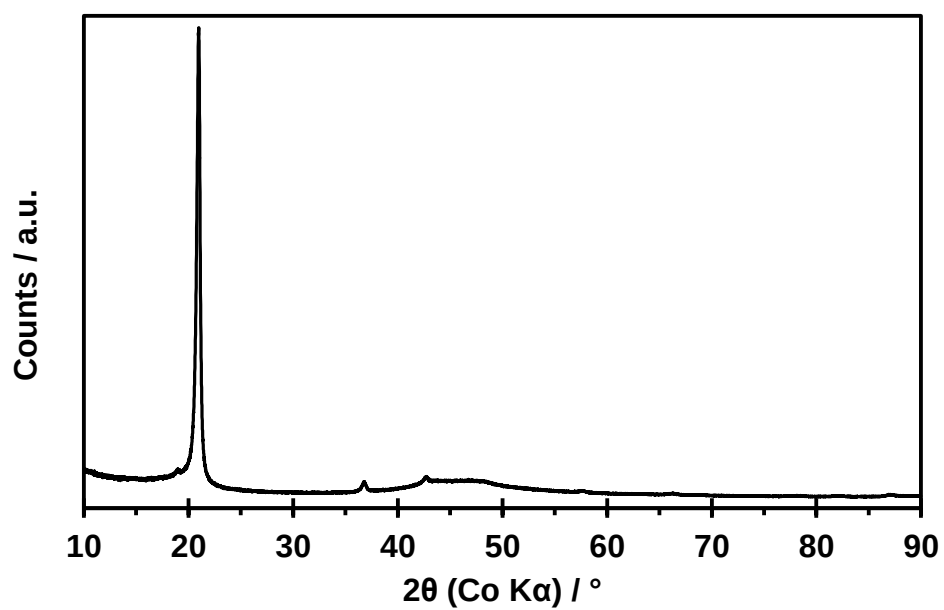


Figure 4. Diffractogram for PTFE.

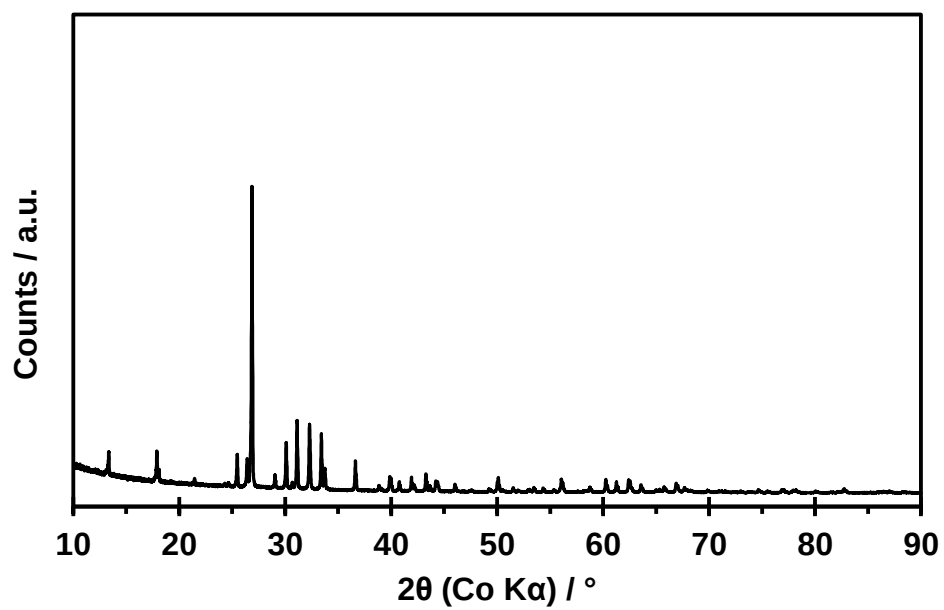


Figure 5. Diffractogram for sulfur.

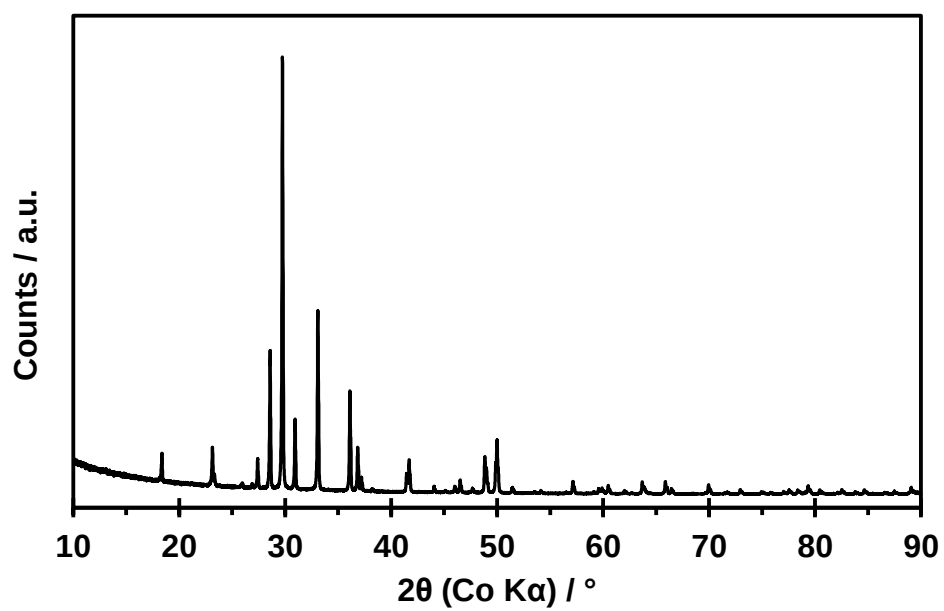


Figure 6. Diffractogram for potassium perchlorate (KClO₄)

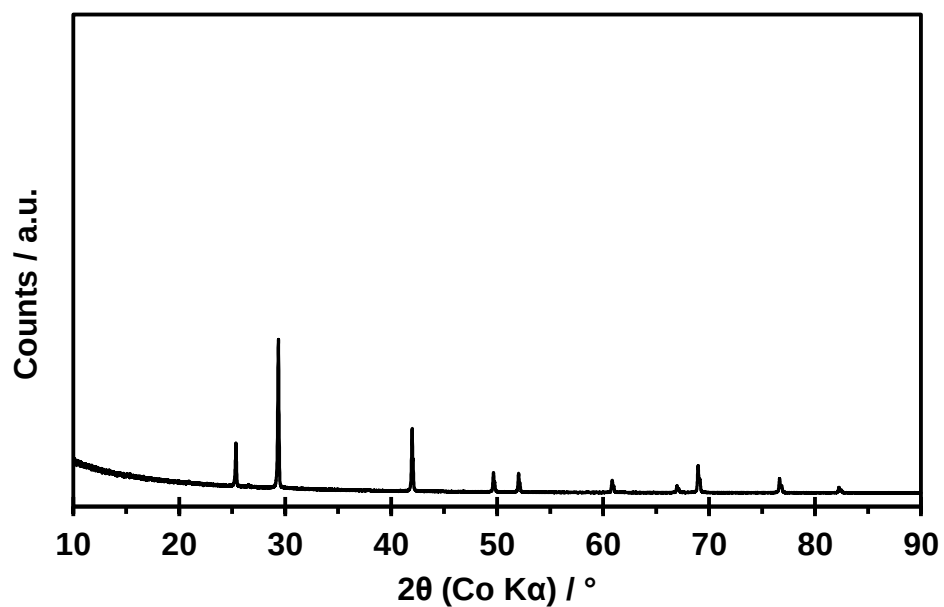


Figure 7. Diffractogram for potassium iodide.

XRF analysis was performed on the fuels used in this study. The major impurities are listed in Table 1.

Table 1. Summarised XRF analysis of aluminium and sulfur.

	Aluminium	Sulfur
	Sample content (wt.%)	
Aluminium	99.59	-
Sulfur	-	98.2
	Impurities (wt.%)	
Magnesium	0.20	0.36
Iron	0.07	-
Silicon	0.04	-
Sodium	0.04	0.23
Potassium	< 0.01	0.05