Imperial College London

Ammonium Nitrate – Fertiliser, Oxidiser and Tertiary Explosive.
A Review of Ammonium Nitrate Safety Issues based on Incidents, Research and Experience in the Safety Field

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THE UNIVERSITY OF QUEENSLAND AUSTRALIA

- Governmental Regulations – Storage and Transport
- Safe Process Operation
- Threat from “Improvised” explosives
- Recent incidents
- Debate around testing of AN
- Novel products
- Increased use of AN based explosives (Chinese economy)

8 months ago: A wedding portrait sits in the rubble of a home that was destroyed by the explosion of a truck carrying ammonium nitrate after it crashed with another vehicle the previous night near Monclova in northern Mexico, Monday, Sept. 10, 2007. The incident killed at least 34 people and injured some 150.

Explosion of fertilizer transporting truck on Monday morning

An ammonium nitrate transporting truck exploded on Monday morning in Romania, Buzau county. The ammonium nitrate is used in the agriculture as fertilizer. 16 persons died, 11 injured. Among the dead there are 7 firemen, 2 journalists and 8 passengers of the cars parking nearby. 1 soldier and 3 inhabitants are missing. The number of the dead is not definite. Due to the explosion the roof of 17 houses damaged, the windows broke. At the site of the detonation an approximately 10 meters deep crater opened. The explosion damaged the pavement of the road on a 40 meter long section. /FigyelőNet.portál 24th May 2004/

Reuters

MEXICAN BLAST: A truck carrying fertilizer has exploded in Mexico, killing dozens and wounding more than one hundred, including rescue workers.

Ammonium Nitrate

Hygroscopic solid and oxidant, Melting Point 169 deg C

“ stable” ***unless contaminants present***

– eg organic species, metallic & other fuels, halides, pH

Known and characterised tertiary explosive

Ammonium Nitrate decomposition chemistry (simplified)

Reversible endothermic disssociation

$$NH_4NO_3(s) \;=\; NH_3(\mathrm{g}) \;+\; HNO_3(\mathrm{g})$$ - ΔH=186 kJ/mole AN

followed by a number of irreversible exothermic reactions at higher temperature e.g.

$$NH_4NO_3(s) \;=\; N_2O(g)+2H_2O(g)$$ - ΔH=-37 kJ/mole AN

$$2NH_4NO_3(s) \;=\; 2N_2(g)+4H_2O(g)+O_2(g)$$ - ΔH=-118 kJ/mole AN

Storage

October, 1918 Morgan, New Jersey
One of the shells released from a shell loading plant explosion caused a large explosion in AN store, but the majority of the ammonium nitrate did not detonate.

1963 Holland – No Injury
4000 tonnes of NPK in storage involved in self-sustained decomposition.

1966 USA – No injury
A fire involving AN fertiliser and other combustibles lead to an explosion

1973 USA – No injury
A fire in an AN wooden store resulted in the explosion of a few tonnes of AN.
14,000 tonnes were unaffected.

1975 Germany – No injury
Self sustained decomposition in NPK fertiliser initiated by welding resulted in evacuation of 1000 residents.

1978 USA – No injury
500 tonnes of AN involved in a warehouse fire – no explosion

1982 UK – No injury
Major fire with wooden furniture stored near AN fertiliser.
Resulted in a deflagration and toxic fume release. Local evacuation undertaken.

Storage contd

1987 France — No injury
Self sustained decomposition in 1450 tonnes NPK fertliser.
Mass evacuation due to toxic fume release but bulk AN not affected

1978 Yugoslavia – No injury
Self sustained decomposition in 17,000 tonnes of bulk NPK fertiliser.
Mass evacuation necessary.

1998 Kentucky, USA
A warehouse containing 4000 tonnes of AN in basement was allowed to burn out. Two explosions reported from propane cylinders stored there. Mass evacuation took place.

September 21st, 2001 AZF Fertilizer Toulouse France 31 fatalities, 350 injuries
The explosion had occurred in a warehouse in which granular ammonium nitrate was stored flat, separated by partitions. The amount is said to be between 200 to 300 tonnes of ammonium nitrate, which is used to make fertilisers. A spokesman for the Interior Ministry in Paris ruled out a criminal attack, saying the explosion had been caused by an accident following an "incident in the handling of products". The exact cause remains unknown in public domain – contamination ?.

Disaggregation

July, 1921 Kriewald Germany (Poland) - 19 fatalities
Workers tried to dislodge 30 tonnes of ammonium nitrate which had aggregated in two wagons when blasting explosives were used the wagons exploded.

September 1921 Oppau, Germany – 450 fatalities
The fertilizer was a 50:50 mixture of ammonium nitrate & ammonium sulphate & the factory had used dynamite to disaggregate over 20,000 times without incident. It is thought that poor mixing had led to certain parts of the mass to contain more ammonium nitrate than others. Only 450 tonnes exploded, out of 4500 tonnes of fertilizer stored in the warehouse.

April 1942, Tessenderlo, Belgium - several hundred fatalities
An attempt to disaggregate a pile of 150 tonnes of ammonium nitrate with industrial explosives ended tragically.

Transport

April 1947, Texas City, United States - several hundred fatalities
A cargo ship was being loaded when a fire was detected in the hold: 2600 tonnes of AN in sacks were already aboard. The captain responded by closing the hold and pumping in pressurised steam. An hour later, the ship exploded and set fire to another vessel, 250 metres away and contained 1050 tonnes of sulphur and 960 tons of AN: this exploded the next day.

July 1947, Brest, France – 29 fatalities
A cargo ship was loaded with 3300 tonnes of AN & various inflammable products when it caught fire. The vessel was towed out of the harbour and exploded.

1954, Red Sea – No Injury
A fire in a ships hold containing AN, paper & organics/ copper resulted in an explosion. The ship was abandoned.

1960, 1963 Traskwood, USA – No Injury
Wagons were derailed with AN, nitric acid & hydrocarbons involved in a fire & explosion.

Transport contd

1965 Atlantic – 3 drowned
4000 tonnes of NPK in bulk storage in self-sustained decomposition.

1967 USA – No injury
A fire involving 50 tonnes of AN in paper bags in wagons with wooden interior was allowed to burn out.

1972 France – 2 fatalities
Decomposition of lagging contaminated with AN & organics lead to an explosion. and release of hot AN solution.

1972 Australia – 3 fatalities
A fire in a semi-trailer with low density AN & oil lead to an explosion.

1997 Brazil - several fatalities
AN truck fire compounded by fire in petrol tanker trying to pass.
A detonation was thought to have been initiated by an exploding propane bottle.
Fatalities were largely in a parked coach near to the fire.

2000 Florida, USA – one fatality
Collision between an AN truck and gasoline tanker resulted in a fire.
(Fatality due to collision).

1994 Terra, Port Neal, US – AN neutraliser

In a 1994 accident, AN solution (about 70 tonnes of AN) exploded during a manufacturing process, causing a number of deaths and injuries. During a procedure to shut down the process, compressed air was applied to the nitric acid line into the neutralizer, followed by pressurized steam at 200 psig and temperatures up to 220 deg C. After the steam had passed through the nitric acid line for several hours, the ammonium nitrate exploded in the neutralizer. The solution was highly acidic and was contaminated by chlorides.

Dust Explosions in Air

AN is basically an oxidant.
It has no measureable dust explosion characteristics
e.g. minimum ignition energy, minimum ignition temperature, KST etc.

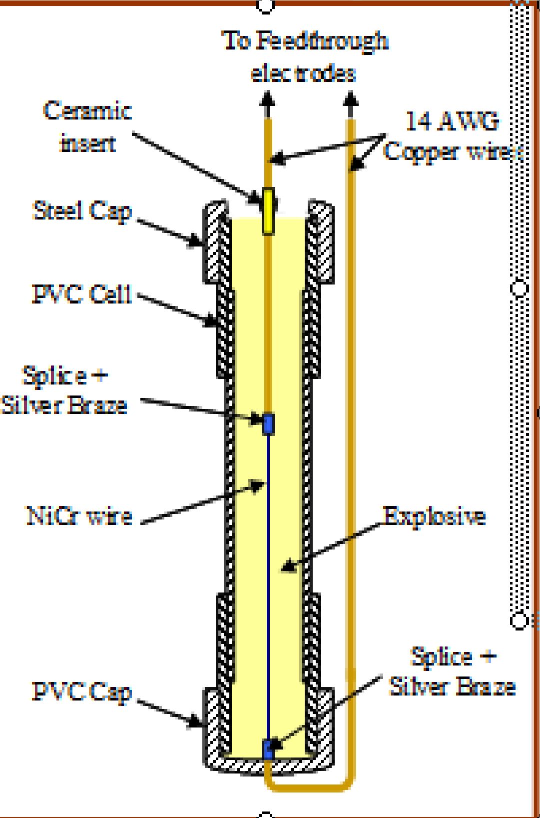
Deflagration and Minimum Burning Pressures

Deflagration – steady state burn of condensed phase media
– pressure dependent with defined cut-off pressure (MBP)
– molten liquid – fizz zone – steep thermal gradients.

A number of studies have been carried out on AN and various additives & stable deflagration of pure solid AN has not been observed < 0.1 GPa

The presence of a halide salt or fuel can reduce this threshold pressure by a factor of 100 e.g. to 10 bara. Molten AN exhibits a lower MBP also

Minimum Burning Pressure Facility - CERL



- 10 cm long straight NiCr wire imbedded in explosive
- 25 mm diameter PVC cell
- Cylindrical geometry
- Cell suspended in 4-L high-pressure vessel

Thermal Explosion/ Reaction runaway

Near simultaneous exothermic reaction - small thermal gradients.

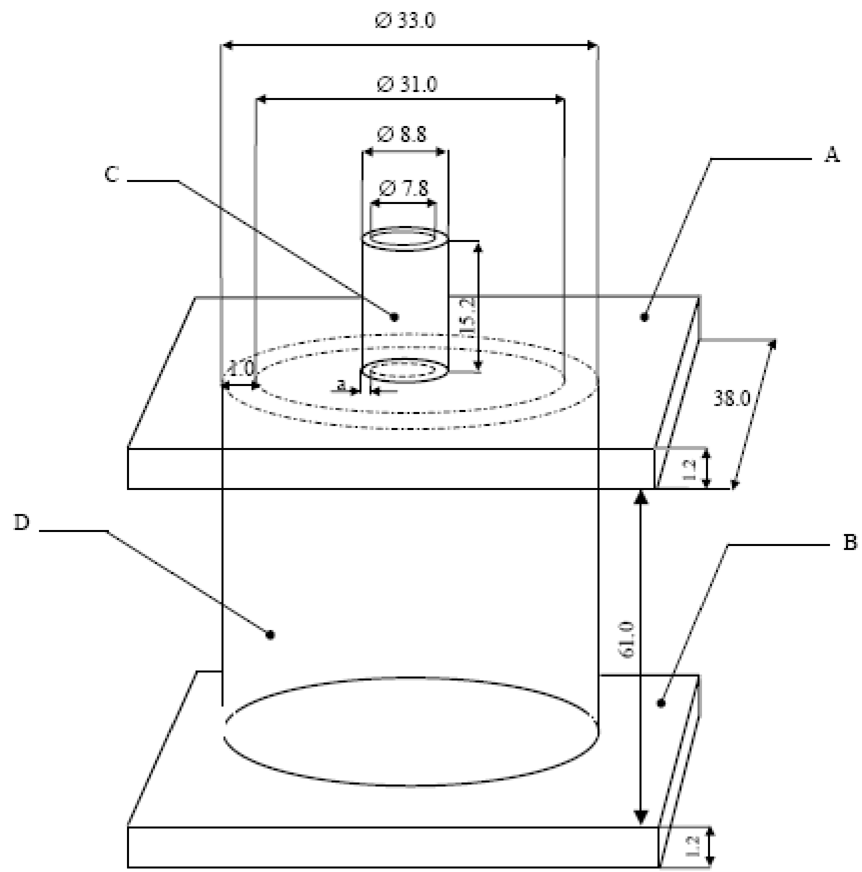
For pure AN, with endothermic & exothermic reaction pathways, onset temperatures for thermal explosion are high, ie ~ MPt.

This onset temperature can, however, be dramatically reduced by the presence of a fuel or catalyst for thermal decomposition.

Detonation, Shock to Detonation- AN as a tertiary explosive

Diameter > critical diameter (density, particle characteristics, confinement)

Shock Stimulus > shock pressure & critical area normally requiring donor charge



(A)	Top plate (Schedule 40 carbon (A53 grade B))
(B)	Bottom plate (Schedule 40 carbon (A53 grade B))
(C)	Steel pipe nipple (a = 0.5 cm), Schedule 40 carbon (A53 grade B)
(D)	Steel pipe (Schedule 40 carbon (A53 grade B))

Figure 18.7.1.1: VENTED PIPE TEST

TNT Equivalence of pure Ammonium Nitrate solid

- assuming 100 % efficiency
- chemical equilibrium
- adiabaticity
- ideal detonation (Chapman Jouguet)

Approach taken

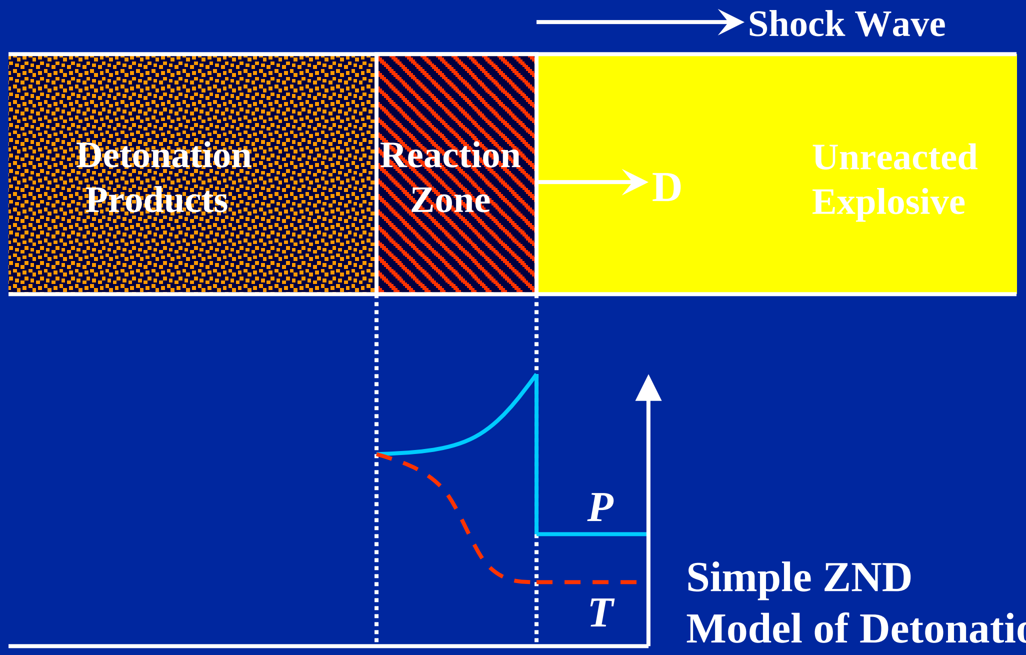
- commercially available ideal detonation computer program
- best fluid EoS
- with/ without water condensation
- range of AN initial densities

Conservative estimate
Solves water condensation issue
Finite rate phenomena not incorporated here

Ideal Detonation Model

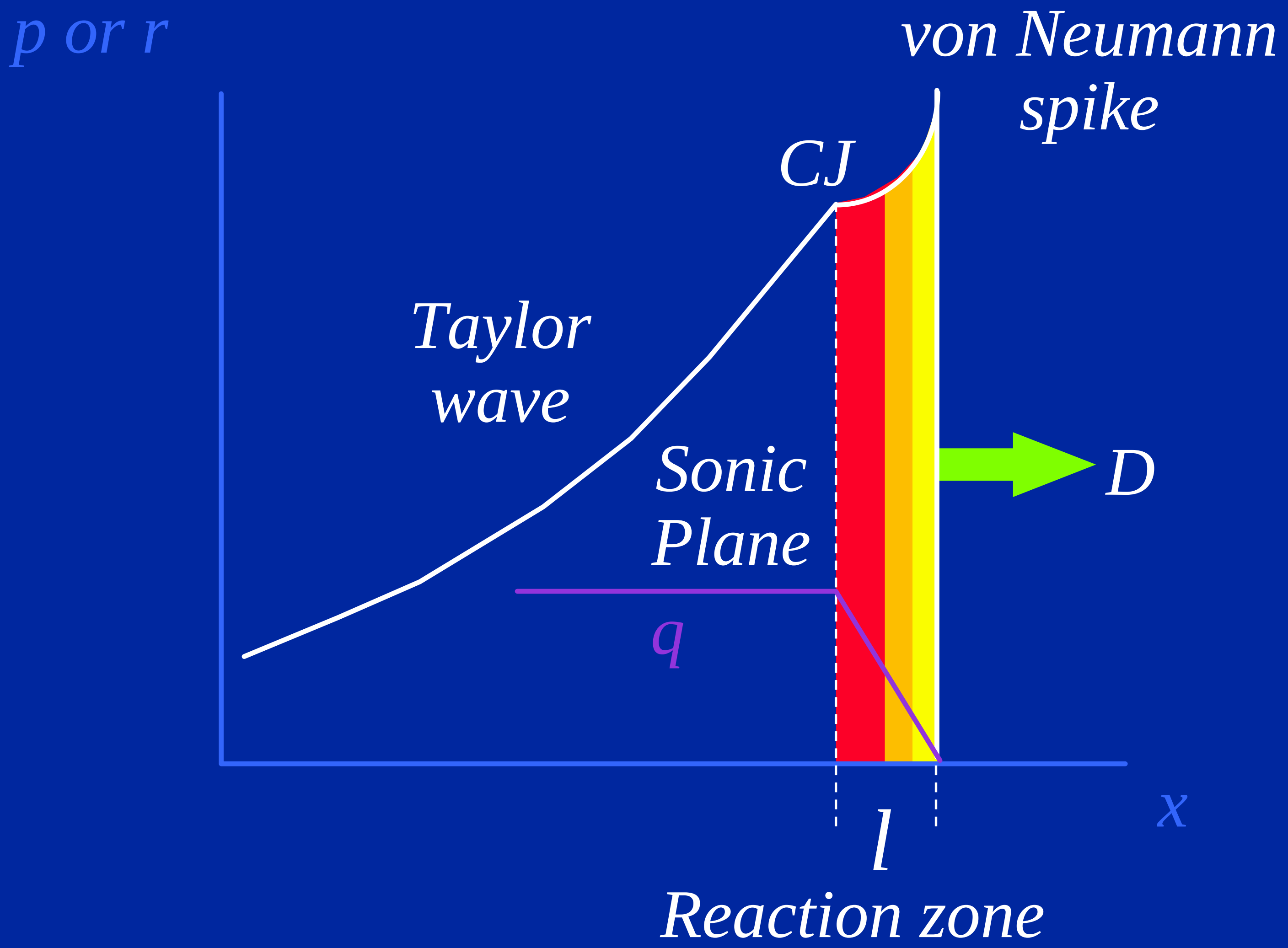
In an idealized model of detonation, explosive performance is dependant on

- equilibrium thermodynamics of detonation products (fluid and solid phases)
- initial density of the explosives
- heat of formation of the explosive



Simple ZND Model of Detonation

ZND Detonation and Rarefaction



Ideal Detonation Computer Programs

- EoS (fluid/ solid) - inter/ intra molecular contributions

- Chemical Equilibrium Algorithm

- Calculation Options

- Databases

    ingredient explosives

    product thermodynamics

- Windows/ GUI etc

Ideal Detonation Codes EoS

Fundamental – WCA or similar –
CHEQ, IDeX, Cheetah, TDS

Based on statistical mechanics – hard sphere perturbation theory

Parameters from other sources

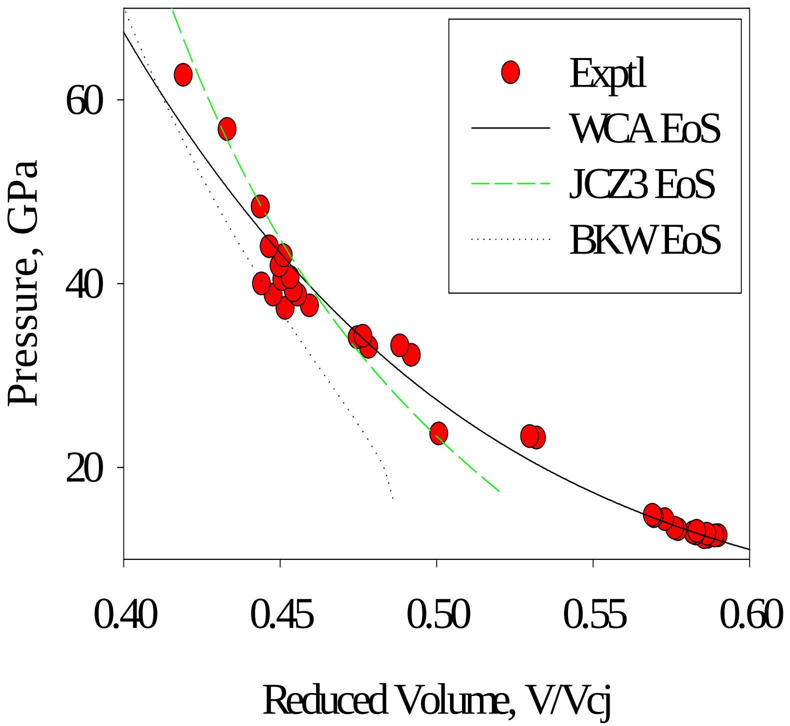
Well behaved higher derivatives

Good match ALL experimental data

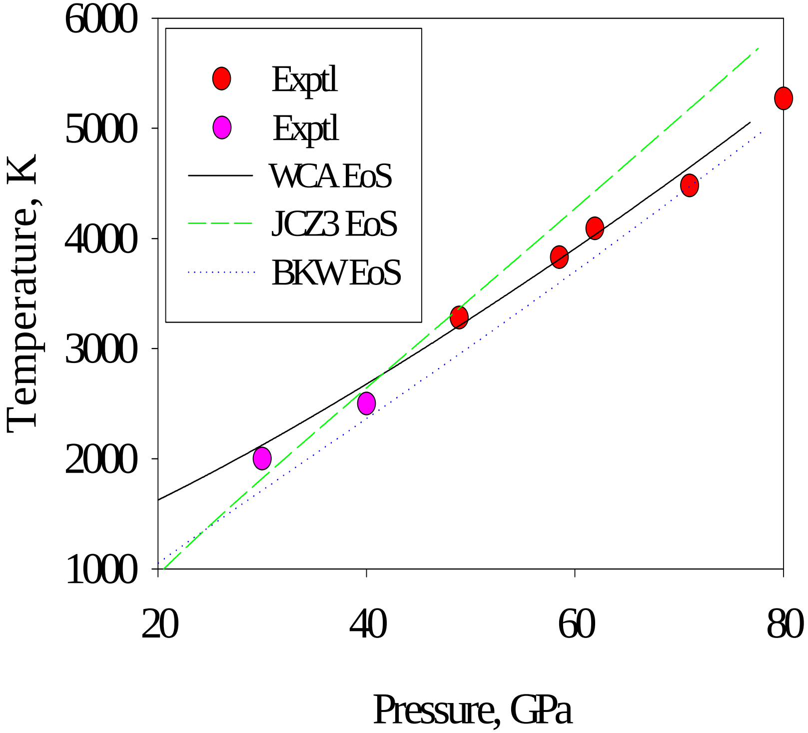
More sophisticated calculation

Some remaining uncertainties

Livermore's largest two-stage gas gun is 20 meters long. Its projectile flies down the barrel at speeds up to 8 kilometers per second to produce a shock wave millions of times the pressure of air at the surface of Earth. Technicians Leon Raper (left) and Keith Stickle are setting up the gas gun for an experiment.



Water Hugoniot: shock pressure

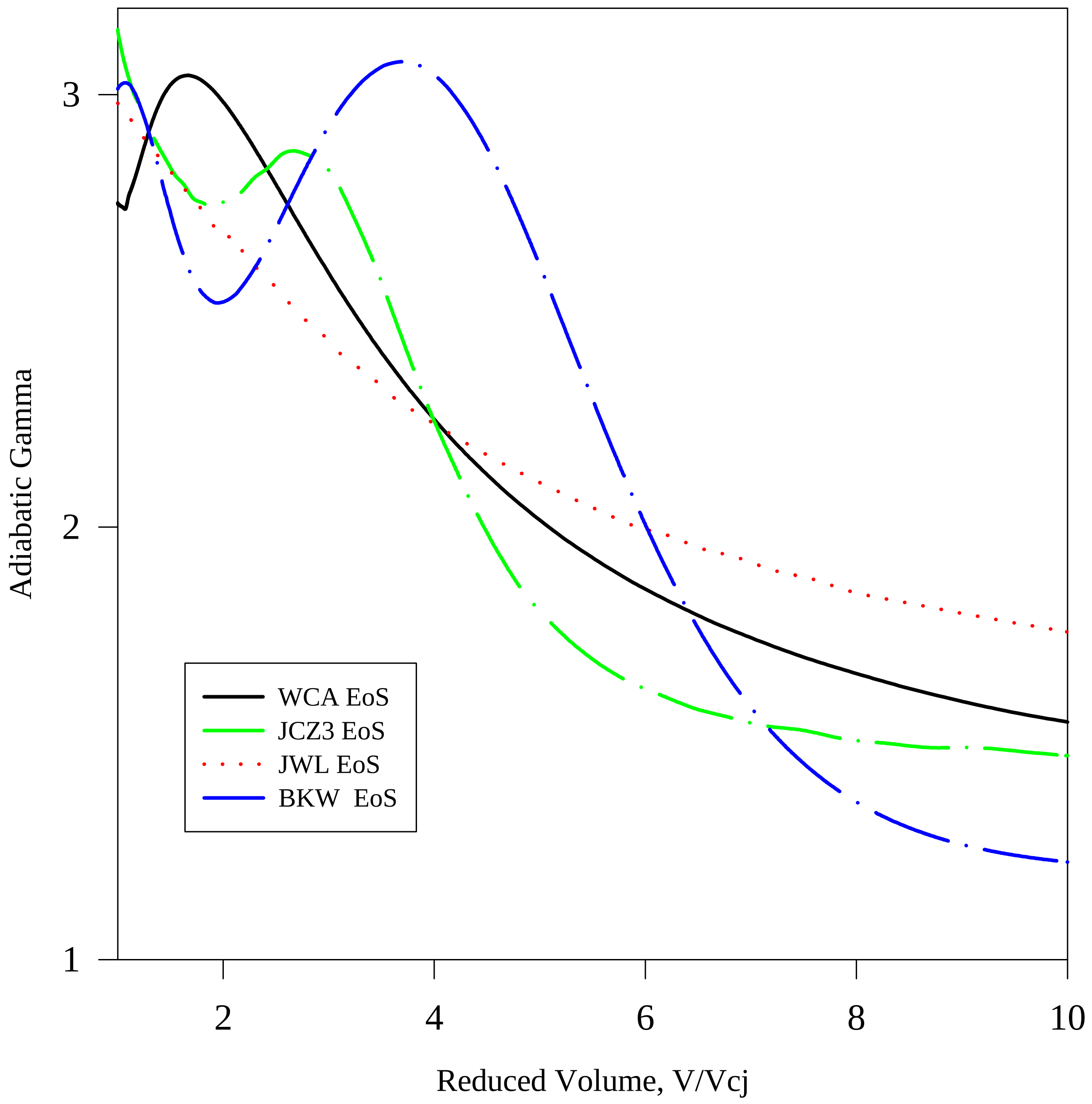


Water Hugoniot: shock temperature

ile Edit View Data Calculation Results Window ?

etonation	1	2	3	4	5	6	7	8
halpy of source reagents at p0=1atm, kcal/mole								
C5H8N4O12/s/	-125.5	-125.5	-125.5	-125.5	-125.5	-125.5	-125.5	-125.5
nsity of condensed source reagents, g/cub.cm								
C5H8N4O12/s/	1.77	1.73	1.7	1.65	1.6	1.55	1.5	1.45
Detonation parameters								
Detonation mode	CJ	CJ	CJ	CJ	CJ	CJ	CJ	CJ
Detonation velocity, km/s	8.33305	8.17468	8.06125	7.88207	7.71477	7.55861	7.40229	7.18324
Temperature, K	4421.53	4455.83	4478.71	4511.35	4537.05	4555.65	4474.68	4514.75
Pressure, GPa	28.7189	27.4496	26.5494	25.1351	23.8126	22.5657	19.5246	17.8804
Density, kg/cub.m	2309.68	2268.66	2237.8	2186	2133.5	2080.03	1967.34	1905.34
Mol.weight, kg/kmole	29.2138	29.2455	29.2702	29.3136	29.3606	29.4121	29.4018	29.2503
Ro/Ro0	1.3049	1.31136	1.31635	1.32485	1.33344	1.34196	1.31156	1.31403
se mole fractions in system, %								
Gaseous phase	93.9603	94.5361	95.0237	95.9518	97.0367	98.2945	100.0000	100.0000
C/s/diamond	6.0397	5.4639	4.9763	4.0482	2.9633	1.7055		
mponent mole fractions of hase "Gaseous phase" in phase, %								
CO2	38.7878	38.2158	37.7258	36.7906	35.7061	34.4731	32.4344	31.6232
H2O	36.4609	36.0498	35.7131	35.0936	34.3949	33.6098	32.7953	33.1829
N2	18.7847	18.6439	18.5300	18.3240	18.0974	17.8504	17.5926	17.6774
CO	3.9230	4.8842	5.6954	7.2241	8.9780	10.9584	13.8797	14.5206
NH3	1.7134	1.7953	1.8536	1.9442	2.0253	2.0958	1.9583	1.5792
H2	0.2378	0.3036	0.3614	0.4763	0.6177	0.7901	1.0940	1.2218
NO	0.0564	0.0588	0.0603	0.0622	0.0632	0.0634	0.0576	0.0755
CH4	0.0352	0.0478	0.0595	0.0841	0.1164	0.1582	0.1872	0.1180
Calculation statistics								
Iterations done	22	20	19	17	16	15	14	14
Precision reached	6.46e-07	6.57e-07	9.39e-07	9.80e-07	5.17e-07	8.33e-07	9.12e-07	8.22e-07
Precision reached (tv)	1.29e-07	1.31e-07	1.88e-07	1.96e-07	1.03e-07	1.67e-07	1.82e-07	1.64e-07

mns: 10



Adiabatic Gamma plots

Table 4: TNT Equivalence for some explosive substan

Substance	TNT Equivalence
Sodium chlorate	0.04
Ammonium nitrate	0.14
High strength hydrogen peroxide	
Dibenzoyl peroxide	0.09
t-butyl-peroxyacetate	0.17
t-butyl-peroxypivalate	0.14
t-butyl-peroxy maleate	0.14
Methyl-ethyl-keytone 60%	0.26
Peroxyacetic acid (40%)	0.05
Teriary butyl peroxybenzoate	0.4
Dibezoyl-peroxy benzoate	0.25
Di-tert-butyl peroxide	0.38

The consensus of opinion on ammonium nitrate hazards is that, in the event of a large fire at an fertiliser store, a pool of liquid ammonium nitrate will be formed at the side of the stack that is nearest to the fire. If this pool is struck by a high speed missile (e.g. something falling or part of a drum that has exploded) then a local explosion will occur sending a shock wave into the main fertiliser stack that has not melted. If this stack contains just less than 300 tonnes it will not support a detonation but will deflagrate and, in doing so, will release an amount of energy equivalent to 41 tonnes of TNT. This figure is calculated on the basis of a TNT equivalence of AN of 55% and an efficiency of 25%. The 6.9×10^3 Pa (1 psi) overpressure hazard range from such an explosion is 600m.

AN TNT Equivalency =

Thermodynamic TNT equivalence

x Efficiency Factor

TNT equivalent (tons)	*Efficiency coefficient*	*Tons of off spec AN involved as reactant*	*Estimated mass stored*	*Proportion of mass of AN involved in the reaction / storage*
20 - 40	*0,3 (AN in accordance to NFU 42.001) to 1 (AN mixed with 6% fuel)*	*20 - 120*	*390 -450*	*5 to 31 %*

Table 1 : TNT equivalence and AN

The TNT equivalent used in the calculation is 0.7, and the ammonium nitrate is assumed to be compressed to a specific gravity of 1.72 (1.72 grams/cm^3).

Explosive	TNT	AN H_2O gas only	AN	AN H_2O gas only	AN
Density kg/m^3	1640	800	800	760	760
CJ Internal Energy MJ/kg	1.7579	-4.15	-4.15	-4.17	-4.17
Internal Energy – 1 atm MJ/kg	-4,890	-6.31	-6.49	-6.30	-6.47
Particle Velocity km/s	2.017	0.914	0.914	0.892	0.892
Energy Release MJ/kg	4.6139	1.742	1.9223	1.732	1.902
TNT Equivalence		**38**	**42**	**38**	**41**

AN TNT Equivalence – Disparity in Estimates

- some results are based on explosion and not detonation state data
- assumptions regarding the composition of detonation products
- different (less accurate) equations of state
- different ammonium nitrate densities
- inclusion of heat loss and/or kinetic energy
- combining efficiency and TNT equivalence in one datum

AN Bases of Safety

- AVOID – contamination, shock and sources of heat >170 deg C
- MITIGATE – compartmentalise hazards to avoid single event
  barriers between inventories, shock absorbers, deflectors
- PROCEDURAL – site security, surveillance
- ELIMINATE – inventories less than critical mass

TNT Equivalence/ separation distances – uncertainties
ambiguities
overly conservative
not economic

More holistic safety approach desirable.

<u>Pure</u> ammonium nitrate

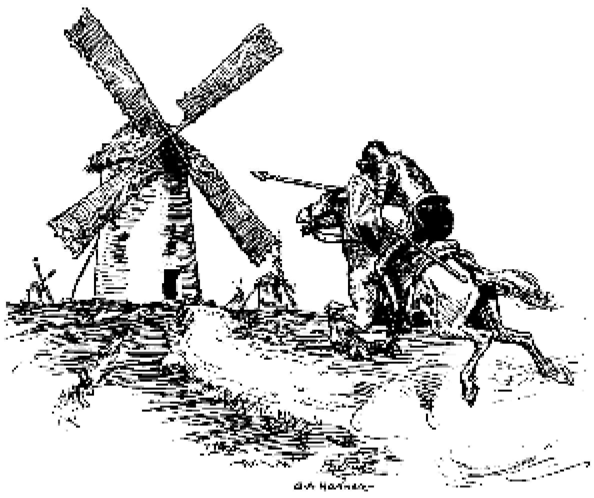
(i) it cannot form an explosible dust in air

(ii) it does not deflagrate until comparatively high pressures eg (~ 0.1 GPa) are reached

(iii) it is thermally stable, even in an adiabatic environment until temperatures >> ambient conditions eg ~ MPt

(iv) Detonation (pure solid AN) requires large shock stimulus and large diameter/ confinement

Concern is contamination, accidental or deliberate.



Don Quixote