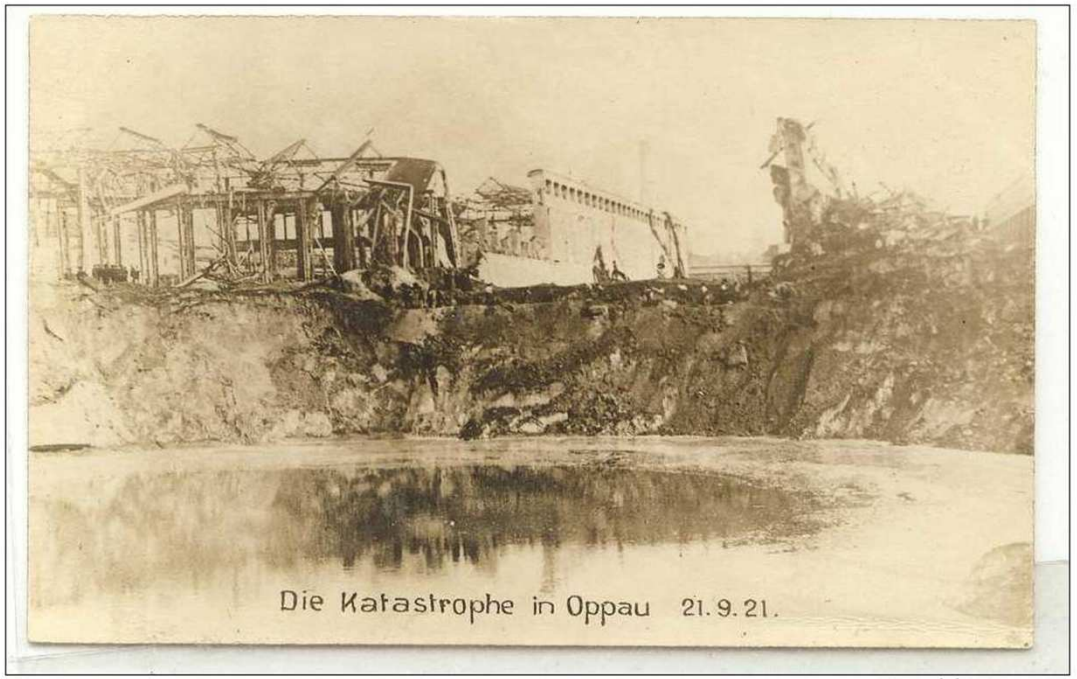
ACCIDENTAL EXPLOSIONS INVOLVING AMMONIUM NITRATE: PHYSICO-CHEMICAL PROPERTIES, SAFETY, INCIDENTS AND MITIGATION OF BLAST EFFECTS

Martin Braithwaite (Cambridge University, UK) & Ronald Peddie (Peddie Engineering , NSW, Australia)

“The very material that was destined to create nourishment and bring life to millions … has suddenly proven to be a savage foe, for reasons we do not yet know.”

Carl Bosch co-inventor invertor of the Haber/Bosch Ammonia process after the Oppau explosion in 1921 [D Jeffreys (2010)]

Oppau 1921



Toulouse 2001

AN use and distribution

- AN is a ubiquitous material
- Worldwide production of 50 Million tonnes
- Among the top 5 of produced chemicals
- Low cost and effective
- No substitutes known

Incident History

- There have been a number of very large incidents involving Ammonium Nitrate
- Oppau 1921
- Texas City 1946
- Port Neal 1994
- Toulouse 2001
- West Texas 2013

- These were devastating and catastrophic incidents
- However the frequency of incidents is low given the vast usage– which speaks to the inherent stability as detailed in this presentation
- Proper application of knowledge should eliminate incidents

AN properties

- The properties of AN pertinent to an explosion incident have been thoroughly studied
- The studies show that at normal handling conditions AN produced to regulation is very stable
- External influence must be applied to lead to an incident

Reaction chemistry

- Primary reaction pathways shown below

$NH_4NO_3(s/l) = NH_3(g) + HNO_3(g)$ - ΔH=186 kJ/mole AN (1)

followed by a number of exothermic reactions e.g.

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

and at higher temperatures still

$2NH_4NO_3(s/l) = 2N_2(g) + 4H_2O(g) + O_2(g)$ - ΔH=-118 kJ/mole AN (3)

AN thermal explosion (cook-off) – I

- Once a molten state is reached AN can support a self-sustaining reaction (CERL paper)
- Quantity, containment and heat loss to environment all factors
- Early reaction is endothermic
- As the early reaction is endothermic it means heat has to be added in some way to start an incident e.g.fire

AN thermal explosion (cook-off) – II

- Although the AN reaction is self-sustaining in the later hotter stages it does not necessarily lead to a thermal explosion
- This would be simply a decomposition of the ammonium nitrate leading to a gas release

AN deflagration and minimum deflagration pressure

- The minimum burning pressures for pure solid Ammonium nitrate are very large
- In normal circumstance they are not relevant to any incidents
- Solid Ammonium Nitrate does not burn or undergo DDT!
- If contamination is present in significant quantities a decomposition can occur

AN shock to detonation

- Laboratory experimentation have shown it is possible to shock initiate pure solid Ammonium nitrate
- However the charges and methods for achieving this require very extreme initiation
- It is unlikely this would be present in an accident without a deliberate act
- Oppau accident - use of explosives to break up agglomerated AN pile

Insults (e.g. Shrapnel, Shock. Heat, Contamination)/deviation from design intent

- The stability of pure AN can be dramatically altered by external deviation.
- Molten Ammonium Nitrate produced by an external fire and generating ags is much more sensitive than pure solid AN
- The introduction of contamination such as halides and other contaminants (reducing agents, fuels, salts of transition metals, acidic conditions) can also render Ammonium Nitrate unstable
- These causes on their own are mostly insufficient to lead to an explosion and another process must occur

Accident causes

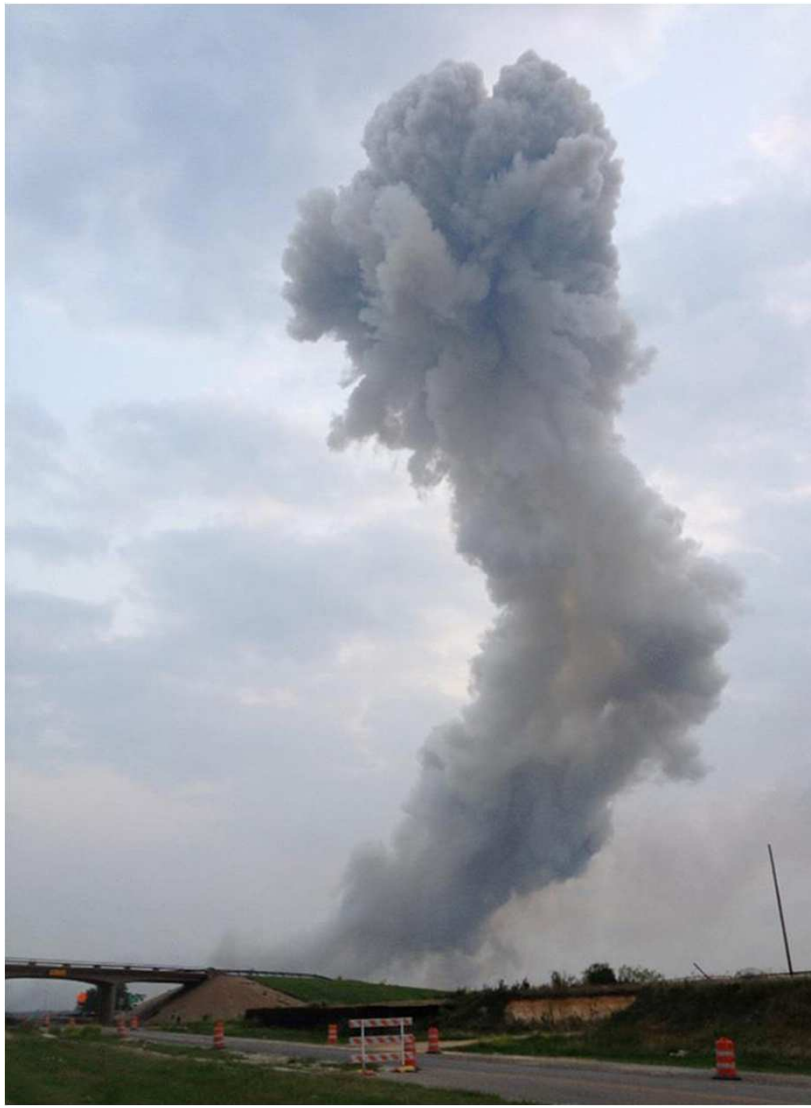
- Accidents involving AN are well documented
- The causes are normally reasonably obvious
- Oppau – the use of blasting to break caked AN – this has not been tried since!
- Texas City -making AN with sufficient fuel to sustain a fire with AN – lead to strict regulation of organic content
- Port Neal – lack of process control - pH
- Toulouse contamination – do not store anything with AN
- West Texas - use fire proof buildings

QD Risk Relations and TNT equivalence

- Overly conservative/ assumptions regarding efficiency and probability of fire/ initiation
- Tertiary explosive, large critical diameter, partial reaction, with no reaction with air
- Should not be subject to same QD as conventional explosives

Explosion Mitigation approaches

- Compartmentalization
- Secondary containment/ bunkering
- Passivation/ stabilization



Plume from west Texas explosion 2013

Societal perceived compared with actual risk: media, legislation

- Incidents involving Ammonium nitrate can be large
- Commentary on the safety of the entire industry normally follows
- Much commentary not accurate (Ref IChem E article), assorted news bulletins (not you tube etc)
- Generally little understanding of financial and instrial importance of AN initially
- Leads to unease about whole industry
- *From the Chemical Engineer UK after the West Texas Accident 2013*
- *Explosion prevention expert however, says that the explosion may instead have been caused when the blaze heated a tank of anhydrous ammonia, causing the vapour to expand and leak out through safety valves. This could then form a huge cloud of ammonia, which when mixed with air can explode. This, he adds, could have also set off the ammonium nitrate stored on the site*.

Summary and conclusions

- The risks involving handling Ammonium nitrate are low
- It is a stable and well understood chemical
- However due to the quantities handled it must always be treated with care
- Any incident blackens the whole industry
- Compliance with existing safe practices is main requirement
- SAFEX and the fertiliser producers have produced good guidelines