# MITIGATING THE CONSEQUENCES OF EXPLOSIVES INCIDENTS – CONCEPTS FOR STORAGE OF AMMONIUM NITRATE EMULSION MATRIX

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## INTRODUCTION

Ammonium nitrate based emulsion matrix (ANE) is frequently stored in large quantities prior to its introduction and gassing as a bulk explosive. It is usually classified as UN 3375, 5.1 Dangerous Goods as it complies with UN tests series 8 (a, b and c). Some countries and state authorities adopt a more stringent standard, classifying the product as 1.5 (very insensitive explosive with a mass explosion hazard). This stricter classification therefore places restrictions of quantities stored and minimum separation distances.

This paper introduces some concepts that are the subject of current investigation that aim to minimize the risks associated with ANE storage as well as mitigating the consequences of any event, however improbable. The primary aim of this work is both to protect the workforce and general public outside the storage zone A secondary aim is to avoid the use of large and somewhat restrictive separation distances required by some authorities by more careful design of storage inventory and blast barriers.
The methodology adopted here has its origins in Inherent Safety concepts used in the chemical and petrochemical industries [T A Kletz].
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## ANE PROPERTIES

ANE can be considered as a void free emulsion though in actual practice some gas void inclusions are inevitable. Typical ANEs comprise an oxygen balanced mixture of supersaturated AN solution, in a combination of oil, surfactant and wax: water is usually present in the range 12-20 % w/w. The medium is normally within a few percent of its theoretical maximum density.

ANE under normal storage conditions is not susceptible to the normal insults that initiate exothermic reaction in high explosives e.g. fall-hammer impact, instantaneous friction, static electricity etc. The only significant hazards are due to:

(i) Shock/ high velocity impact – density dependent

ANE has a large critical diameter for stable detonation, even under confinement. Clearly when gassed, this diameter reduces to the few centimetres of a sensitized emulsion and this will be further reduced on heating and loss of water

(ii) Heating (thermal explosion) – become far more hazardous with water loss

Water contributes a substantial barrier to overheating due to its substantial heat capacity and latent heat of evaporation. Once the water content is reduced (~140 deg C) there is the possibility of exothermic reaction

(iii) Heating (thermal deflagration) – only when contaminated or having loss water
Under normal conditions ANE has a large minimum deflagration pressure (> 10 bara [Ref]) and will not deflagrate under normal storage or manufacturing conditions. This minimum deflagration pressure is much reduced when water is lost or the temperature raised

## DEVIATIONS FROM DESIGN INTENT

ANE can more readily undergo exothermic reaction when heated or contaminated. ANS (Ammonium Nitrate Solution) exothermic decomposition is catalysed by a range of reducing agents and acidity e.g. organic material, transition metals and salts, halide containing species, and reducing agents). In the event of gas void formation, ANE properties will revert to a standard sensitized emulsion and become significantly more shock sensitive. In addition, if overheated for a prolonged period water will be driven off and the remaining media will behave as a molten ANFO in terms of deflagration and detonation properties

In the continued and assured absence of such excursions, be they accidental or deliberate, ANE storage can be regarded as safe. The safety case, and its acceptance by the regulatory authorities, is however dependent on these assurances.

## INHERENT SAFETY CONCEPTS

An inherently safe process [Kletz] is one that cannot lead to an accident, irrespective of disturbance. The aim of inherent safety in the context of process and storage design is to render the inventory less hazardous and of smaller size and the process simpler without heavy reliance on external monitoring and protective measures.

In the context of ANE some of the keywords used in inherent safety studies are discussed here.

*Avoid*

Inevitably a balanced oxidizer/ fuel system poses a hazard. This might be reduced as follows – if practicable:

- In situ emulsification on introduction to borehole – separate oxidizer and fuel
- Use coarser emulsion with high water content and lower acidity

*Reduction/ Intensification*

Inventories of stored ANR should be just sufficient for purpose.

- Minimize inventory of ANE

*Substitution*

Consider less reactive or volatile ingredients.

- Consider use of less reactive or more thermally stable oxidizers and less volatile fuels

*Moderation/Attenuation*

Avoid crystallization but keep temperatures as low as possible,

- Control temperatures nearer the emulsion fudge point
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*Simplification*

"What you do not have will not leak or need maintenance"

- Use gravity flow instead of pumps
- Avoid complex monitoring/ trip systems e.g. bursting discs instead of relief valves

## ACCIDENTS INVOLVING ANE

There have been a number of incidents with ANE, largely while being transported in vehicles involved in road collisions. Of more significance here is the 1994 Porgera explosion in Papua and New Guinea [Ref] where, in a secondary explosion, 80 tonnes of AN exploded following a fire under the storage unit.

## QUANTITY-DISTANCE RELATIONS: TNT EQUIVALENCE

TNT tables and TNT equivalence criteria are routinely used to provide a reliable, if conservative, estimate of minimum separation distances between storage units and site boundaries. This approach assumes a point, instantaneous and complete explosion and this provides a good estimate for high explosives but perhaps less so for the more slowly reacting heterogeneous media used in commercial explosives operations. In adopting this approach for ANE one is making the assumption that it has become sensitized and can undergo near complete reaction instantaneously.

The normal analysis includes a limited allowance for mitigating measures that might be employed, perhaps because of their unproven efficacy. It also affords an opportunity for multiple storage units (suitably separated to avoid domino effects) as overpressures and shrapnel damage will not be additive for discrete events.

## APPROACHES TO EXPLOSION MITIGATION

If a departure from design conditions e.g. Overheating or contamination (accidental or deliberate) cannot be eliminated then an explosion mitigation strategy has to be implemented. The challenge here is to find approaches that are effective but not totally reliant on very large minimum separation distances based on inventories and total available energy therein. Damage due to explosions can be caused by a combination of shock or overpressures and rarefaction waves, fire (including thermal radiation) and shrapnel.

If adopted bases of safety cannot discount thermal, shock or contamination insult then there remains some measures that will mitigate against the worst consequences of an explosion. The damaging consequences of explosions include fire, shock and overpressures, shrapnel, rarefactions and toxic release to ground or atmosphere. The effects of explosions may be compounded by domino effects (sympathetic secondary explosive events initiated by a first explosion) on a production or storage site.

The consequences of any explosion involving ANE might be mitigated by the following approaches.

### Compartmentalization – individual silos

This is a balance between risk involving a number of silos and consequence of a single larger explosion. If used in conjunction with effective barricading it affords an opportunity to reduce overall separation distances and is worthy of a quantitative risk analysis.

### Material of construction of silos

Many ANE tanks are of stainless steel construction, affording strength and eliminating any corrosion... In recent studies [Kuosanen] it has been shown that the consequences of a reaction runaway in a tank containing ANE is far more severe than one made of Aluminium. Aluminium tanks are of lower strength and readily rupture under stress at elevated temperature, thereby avoiding the very high rates of pressurization in the later stages of the thermal explosion process.

### Secondary containment/ bunkering – secondary/ tertiary containment

One major component in our current developments is to design effective barricading/ bunkering from a-priori modelling for worst case detonation. This interdisciplinary study involves a combination of computation fluid dynamic/ material response modelling, design of barricades for shrapnel, overpressure and fire as well as extensive testing and trials. The aim here is to have an established and accepted design basis which may then be used to re-visit the over restrictive minimum separation distances imposed by unconfined detonation assumptions.

### Fusible materials/ frangible seals – rapid release & avoidance of explosive loss of containment

This takes the earlier work of using Aluminium tanks a stage further by introducing materials that are readily deformable once an unsafe temperature is reached. With a controlled loss of containment under conditions well short of the final thermal explosion temperature, hot ANE will be deposited in a state where it will not readily deflagrate. For other than severe fires, it is expected that the large thermal mass of the matrix will extinguish a fire below the tank.

### Releasing or blanketing (water, alkali solution) contained inventory before loss of containment and reaction runaway

ANE is unreactive below an elevated temperature i.e. it will not deflagrate or thermally explode. In the event of an excursion from design conditions it might be possible to lower the temperature of the stored AN and slow AN decomposition using a combination of water (preferably slightly alkaline).

## SUMMARY AND CONCLUSIONS

ANE is unreactive under normal storage conditions. When they are excursions to higher temperature due to external heating or fire or internal contamination ANE can explode, deflagrate or even detonate. The use of inherent safety concepts can limit the hazard. Current research on mitigation the effects of blast will assist in the reduction of conservative minimum separation distances without compromising the safety of plant personnel and the general public.

## LEARNING POINTS

1. ANE under normal storage conditions is unreactive
2. ANE subject to thermal insult or contamination becomes reactive without intervention this can lead to thermal explosion, deflagration or even detonation
3. Current philosophies based on worst case TNT table analysis are going to be safe but overly conservative
4. Measures exist both to reduce the hazard and consequences on ANE storage incidents
5. Current research is looking at two areas – rapid venting of overheated ANE and barricade design

## REFERENCES

T A Kletz

SAFEX Newsletter – Downer CEO

Kuosanen (2007)

Porgera (1994)

Deflagration properties of ANE