

AN solution manufacture product and safety issues for emulsion plant consumers

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Introduction

Discussion about ANS (Ammonium Nitrate Solution) at the last SAFEX congress in Helsinki showed that many people were unaware of some of the production issues in the manufacture of ANS which could affect Emulsion manufacture.

This paper only covers the use of ANS (Ammonium Nitrate solution) manufactured and dispatched directly as a liquid. ANS can also be made by redissolving solid AN, however redissolving AN has a myriad of other problems which would be best discussed in a separate paper.

Summary

ANS is the main raw material for emulsion explosive manufacture. The safety and cost of the emulsion manufacturing process is affected by the specification of the ANS manufacture.

Attention should be made to the specification and control of ANS pH strength, temperature and control of contaminants. The issues of each of the parameters is discussed in this paper.

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Description of Ammonium Nitrate Solution manufacture

Ammonium Nitrate is the main raw material for all bulk explosives manufacture. It is a chemical produced in huge quantities.

Ammonium Nitrate for use in emulsions is manufactured for Ammonia gas and weak (around 60%) nitric acid.

Using Ammonium Nitrate Solution to make emulsions can be a very efficient process. There is no solids handling, dissolving, wastewater, waste bags etc. when using ANS.

ANS is about the fourth or fifth top chemical by tonnage produced in the world. Its major use is as a highly effective nitrogen fertiliser, but the most rapidly growing use is an explosive raw material now accounting for around 20% of world production up from about 5% 40 years ago.

The neutralisation of Nitric Acid with Ammonia is one of the fastest known reactions, an instantaneous and highly exothermic reaction.

The neutralisation reaction to ammonium nitrate is straightforward:



It is an acid - base reaction- so therefore neutralisation.

When ammonia gas is introduced into a liquid stream containing nitric acid a vigorous exothermic reaction takes place leading to the formation of an aqueous solution of ammonium nitrate. All the species formed are ionic and exist in solution as ion pairs. Some of the ammonia and nitric acid molecules may remain unreacted since the high ionic strength of the solutions prevents diffusion of the molecules together. The translational motions of the unreacted molecules are restricted because they weakly associate with the ion pairs as a result of hydrogen bonding mechanisms.

There are many styles of neutralisation, circulation loops, pipe reactor, tank reactor etc.

This note is not about the reaction methods, though that is a fascinating subject [1] .

All the reactors do the same duty, they take Ammonia and Nitric acid in and produce ANS at the end – so from the customer perspective the type of reactor is irrelevant.

I want to discuss the properties of the ANS product especially for those who make emulsions and how these are realised on the neutralisation chemical plants.

General safety advice on handling ANS

There are physical and chemical dangers in handling ANS. These are not the subject of this paper but are the topic an excellent and comprehensive guide from Fertilisers Europe. [2]

https://www.fertilizerseurope.com/fileadmin/user_upload/publications/tecnical_publications/guide_nce_tech_documentation/New/Hot_Ammonia_VJ_05112014.pdf

Role of Ammonium Nitrate in Emulsion explosives

Ammonium Nitrate is about 70 - 75% of the mass of an emulsion explosive. It supplies the required oxidiser portion of the emulsion explosive and therefore most of its explosive capability.

Ammonium nitrate is manufactured in large quantities and at low cost. There are no practical alternatives.

Issues of strength

ANS is used in emulsion manufacture at about 76% strength.

The strength of solution produced inside the chemical plants depends on the inlet acid strength and temperature and handling of the internal condensate produced by the plants.

Modern plants can produce high strengths of between 94 – 96%. This strength is reduced before transport as ANS solution.

The limit on ANS strength for transport for UN DG code is 92%. Very often a concentration of 81 – 83 % is used in transportation.

When deciding strength for transportation, it is worthwhile to note the neutralisation plant can often provide very pure water for dilution and this could be transported with the ANS. This could avoid the need for separate water supply to an onsite emulsion plant at the same time ensuring water quality.

However higher strength ANS will attract a lower transportation cost per tonne – so the strength of transport is an economic decision.

Lower strength ANS also can be transported much longer distances without fudging.

So, the supply strength can be optimised on customers' needs and transport and handling costs.

ANS pH

ANS pH is very important for the chemistry of emulsions. Generally, a slightly acidic ANS with a pH of around 4.5 (at 10% dilution) is preferred.

For the neutraliser operators, pH shows the completion of the reaction. pH can swing very easily on a neutraliser from very low to high. So, vigilance is needed by the plant operator to keep it in specification.

ANS pH is the outcome of the ratio of NH_3 and HNO_3 in the neutraliser. There is no cost for the producing plant to adjust pH, but this can be an expensive and time-consuming exercise for emulsion plant. So, an emulsion plant should try to get ANS as close as possible to the final requirement.

Transport regulations mandate pH. Typically, 5 – 7 at 10% dilution. However, there is little danger at pH levels slightly below these levels, so the regulation specification is just rule based.

Low pH often mentioned as a danger source, but this is in manufacture at very extremely low pH say less than 1 and at high concentrations and temperatures.

A 'real' high pH of ANS is not physically possible, however it is possible to get a high pH reading. Above the neutral point NH_3 is not held and will come off as a gas. Neutral pH is about 5.4 – 5.6 (depends on dilution). You can smell ammonia if the ANS is above neutral. So, tankers arriving with ammonia smell or ammonia coming off ANS tanks shows over ammoniation. The reading for ANS will show above the neutral point, but over time ammonia will release and the pH will drift back to neutral pH.

For emulsion manufacture ANS just below neutral, about 4.5 at 10% dilution, is ideal – means less need to adjust the pH down on site for the manufacture of emulsions. There is no advantage in adding NH_3 above the neutral point – it will just flash off as gas.

A problem with high pH's is they must be adjusted with large additions of inorganic acids or in extreme cases strong acids, nitric or sulphuric. Strong acids are hazardous to handle. It is safest and most economical to have the ANS pH close to the requirement for emulsion manufacture.

In some jurisdictions there may be limits on dispatch pH.

Temperature

The initial manufactured temperature of ANS is much higher than needed for emulsions manufacture, more than 150°C typically. This must be reduced to make emulsions by cooling and dilution.

There is a potential danger if you cool high temperature ANS with water jackets in an emulsion plant as there is always the potential to generate steam and over pressurise equipment. You also must consider if boiling is a danger. If this is not considered, a design could even be illegal under pressure vessel code.

Higher temperatures of ANS allow tankers to travel long distances and still be unloaded easily.

So, the best temperature to transport and distribute ANS is again a matter for discussion, the producing plants will always have to cool and dilute.

Contamination

ANS should be clear when above the solidification point and pure white when cooled and solidifying.

There is a very high mass rate of production in an ANS plant so gross contamination is unlikely and difficult simply by volume of product being made. The raw material ammonia and nitric acid are very pure with few avenues for contamination.

Red solution is the most frequent problem. Turning solution red is quite easy if steel or stainless steel is corroding in the neutralisation plant. A human eye detects iron contamination with incredible sensitivity. Sometimes below the level of detection by analysis. So, a 1 ppm level of iron looks red a 5ppm level looks bright red and 20 ppm looks like a sludge.

There is no evidence that iron at these levels cause problems in emulsion manufacture, but it is very obvious and is not a good look.

Role in emulsions manufacture trouble shooting

I think ANS is very often an unlikely candidate for emulsion manufacturing problems.

ANS dispatched as liquid straight from neutralisation is unlikely to have contamination levels which affect the stability of emulsions.

If ANS made from redissolving solid or contaminated streams are used for dilution it is more likely to cause problems in emulsion manufacture.

References

- [1] UNIDO and TWA, Fertilizer Manual, Dordrecht : Kluwer Academic publishers, 1998, p. Chapter 8.
- [2] Fertilisers Europe, "Guidance for the storage of Hot Ammonium Nitrate Solutions," Fertilizers Europe, Brussels, 2014.