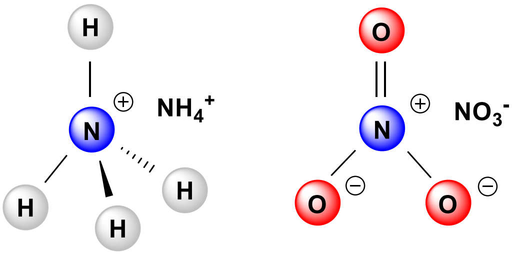
DEPARTMENT OF CHEMISTRY

UNIVERSITY OF OXFORD

Ammonium Nitrate, a simple fertiliser, or dangerous explosive?

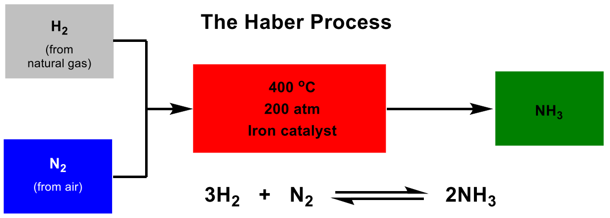
By Alan Tyldesley, MA Chemistry, Trinity, 1974, subsequently Chartered Engineer, Institution of Fire Engineers.

The addition of minerals to crops has been an important part of farming for as long as humans have been cultivating plants. Historically, farmers had to rely on bird droppings (guano) which often had to be collected from remote places. However, since the advent of synthetic fertilisers, this has become unnecessary and crop yields have increased significantly. The key component in fertiliser is nitrogen, without which the plant cannot produce essential compounds such as chlorophyll. One of the most effective synthetic fertilisers in use today is ammonium nitrate.



Ammonium Nitrate

Ammonium nitrate (NH_4NO_3) is an ionic compound containing NH_4^+ (the ammonium ion) and NO_3^- (the nitrate ion). The efficacy of this compound as a fertiliser is owing to its high nitrogen content (35%) which means that it has more value as a source of nitrogen than alternative fertilisers such as calcium nitrate, $Ca(NO_3)_2$ (17% nitrogen). Commercial production began in 1910 and was first made possible by the development of the Haber process. The application of both high pressure and temperature, alongside a specific catalyst, enabled the fixing of nitrogen from air to form ammonia (NH_3) by reaction with hydrogen.


The Haber Process

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

Oxidation of ammonia produces a range of nitrogen oxides, one of which, NO_2, is dissolved in water to form nitric acid (HNO_3). Ammonium nitrate is then easy to make: an acid-base reaction between ammonia and nitric acid produces water-soluble ammonium nitrate, which is dried and formed into pellets ready for transport.

Formation of Ammonium Nitrate

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

However, the storage of this compound is incredibly important as changes in pressure or temperature can both cause decomposition to occur. Ammonium nitrate has two temperature-dependent decomposition pathways: at lower temperatures, nitrous oxide (N_2O, also known as laughing gas) is released; at higher temperatures the ammonium nitrate acts as an oxidiser, releasing oxygen which will readily react with any combustible material.

Decomposition Pathways

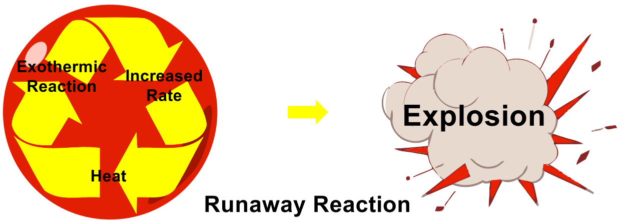
Low Temperature:

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

High Temperature:

$$2NH_4NO_3 \longrightarrow 2N_2 + O_2 + 4H_2O$$

As this reaction is exothermic, the heat produced drives the ammonium nitrate to decompose faster, releasing more oxygen and resulting in an uncontrolled runaway reaction.



Runaway Reaction

Unfortunately, since production began, this decomposition pathway has resulted in multiple serious ammonium nitrate explosions.

In 1911 the chemical company BASF (Bayerishe Anilin und Soda Fabrik) began manufacturing ammonium sulphate ($(NH_4)_2SO_4$) as a fertiliser at their site in Ludwigshaven on the river Rhine. During the war sulphur supplies became short, so they started to make a combined product of ammonium sulphate and nitrate. Unfortunately, this mixed product tended to absorb water and compress into a very solid cake, particularly when stored in large quantities. This material could not be easily discharged from the storage silo so after small-scale safety testing, loosening of the product 'cake' was achieved using dynamite. On 21st September 1921, one such small dynamite charge triggered the explosion of a 50,000-tonne silo, followed moments later by a second nearby. The blast spanned an area of over 10,000 square metres, forming a crater 19 metres deep and resulting in over 500 casualties.

Another violent explosion occurred in 1947, in the port of Texas City, USA where two ships containing over 3,000 tonnes of ammonium nitrate were docked in the harbour. The ammonium nitrate stored on these vessels was formulated, meaning the active ingredient was combined with other substances, in this case highly combustible petroleum jelly and petroleum wax. A smouldering fire was noticed at 8 am in the hold of one ship and fire crews were immediately called. Despite this intervention, the ammonium nitrate detonated with catastrophic consequences soon after and the official fatalities came to 567, including 28 out of the 29 members of the city fire brigade.

Ammonium nitrate made world headlines again in August 2020 when 2,750 tonnes exploded in the port city of Beirut, Lebanon. The cargo had been unloaded from an unsafe ship and stored in a warehouse at the dockside for six years while legal arguments prevented it being moved or used. It is believed that the explosion was triggered by a fire which had started in a nearby stack of fireworks and the second blast was so strong, the explosion was heard 250 kilometres away in Cyprus. The final death toll was 200 people with over 6,500 more injured.

Whilst most ammonium nitrate is made as a fertiliser, it is also widely used as a cheap explosive, especially for mining and quarrying. Formulation with a combustible material such as diesel fuel produces a mix called ANFO (ammonium nitrate fuel oil) which is usually prepared at the point of use. ANFO is quite resistant to explosion and needs a substantial booster explosive so accidental explosions are rare. However, serious security measures are required by these facilities, both to secure the safety of staff, and prevent theft of the prepared explosives.

As a result of these incidents and concerns, there are stringent regulations surrounding the manufacture, storage and use ammonium nitrate. As with many explosive compounds, physical form, such as density, and trace chemical contamination can strongly influence both the sensitivity to explode, and the power of the explosion. Manufacturers must comply with strict controls over purity and industrial processes, including keeping stack sizes small, and ensuring no combustible material is kept nearby. Customers must apply for a licence to use ammonium nitrate and provide appropriate levels of training for staff and security to prevent theft.

Despite the many risks associated with ammonium nitrate, its utility as both a fertiliser and a mining explosive have made it industrially indispensable.