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Ammonia Emission Abatement in a Fluid Bed Urea Granulation Plant

First Commercial Application

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Avant Propos :

Hydro Fertilizer Technologie BV (HFT) est le bras de licence de la grande usine d'engrais azotes Hydro AgriSluiskil BV (HAS) appartenant à Norsk Hydro ASA aux Pays Bas. HFT est leader mondial du marché de la technologie de granulation d'urée en lit fluide depuis le début des années 80.

Krupp Uhde est un des principaux contractants pour la conception, l'engineering, la fourniture et la construction de sites complets de production d'ammoniac – urée.

Krupp Uhde a été pionnier dans l'introduction de la technologie de la granulation en lit fluide HFT dans le monde des engrais azotés.

Cet exposé commun est un exemple parfait de la collaboration étroite des deux entités.

A – FOREWORD :

Hydro Fertilizer Technology B.V. (HFT) is the licensing arm of the large Hydro Agri Sluiskil B.V. (HAS) nitrogen fertilizer plant owned by Norsk Hydro ASA in the Netherlands.

HFT is the market leader in fluid bed urea granulation technology world-wide since the early 1980's.

Krupp Uhde is one of the leading contractors for design, engineering, procurement and construction of complete ammonia - urea production sites.

Krupp Uhde has pioneered the introduction of the HFT fluid bed granulation technology in the nitrogen fertilizer world.

This joint paper is a perfect example of the close co-operation of the two entities.

B - GENERAL DESCRIPTION

I. Introduction: Fluid Bed Urea Granulation development at Hydro Agri Sluiskil in the Netherlands

The nitrogen fertilizer plant at Sluiskil near the estuary of the Schelde River in the south of the Netherlands is owned since 1979 by Norsk Hydro.

Since then it became a world-scale ammonia production site with a capacity of more than 4500 MT, mostly converted to ammonitrate fertilizers but also to urea with a daily capacity of circa 2400 MT as solid urea (prills and granules), as solid urea-ammonsulfate and as urea-ammonitrate solutions.

Urea Technology Developments at Hydro Agri Sluiskil

Sluiskil has a long-standing history in the development of urea as the most important industrial nitrogen fertilizer product.

Since the late 1950's, 6 prilled urea production units have been built on the site. This development abruptly stopped in the early 1970's when urea production moved closer to its markets and/or its new feedstock sources (mainly natural gas).

Small amounts of formaldehyde were injected in the concentrated urea solution prior to the final evaporation stage to improve the crushing strength of the prilled urea, which was also coated with urea-formaldehyde condensates and cooled.

Even with those features, urea prills remain sensitive to handling damage since:

- a) the crushing strength of prills is low ;
- b) the shatter resistance to bulk piling is poor ;
- c) the caking protection is lost in the fracture areas appearing after all handling damage underneath the surface coating layer.

The major disadvantage of prilled urea however remained its small size.

Contrary to other fertilizers, urea cannot be prilled to larger size because it has a very high crystallization heat.

This limitation kept prilled urea out of the high quality bulk blends where size compatibility is essential.

In the United States and in Canada, the industry moved to granular urea by the spherodizer process where formaldehyde-based components were also applied as additives to improve product quality and control dust formation during the manufacturing process.

By then the unit capacities of urea synthesis plants had reached above 1500 MTPD, where multiple spherodizers with unit capacity of 300-400 MTPD had to be aligned.

The Sluiskil management decided to develop its own finishing technology, which would not be limited in unit capacity: the **fluid bed urea granulation**.

II. Fluid Bed Granulation Mechanism

Contrary to prilling or spherodizer granulation, the fluid bed process is able to evaporate residual moisture from the already shaped solid material, thanks to the extensive contact between the surface of each particle with its fluidizing air at high and uniform temperature.

This can only be achieved with a highly efficient additive which forms a liquid phase in the right quantity to retain the structure of the solid particles but still allows the residual water to boil out of this liquid phase.

Formaldehyde has proven to be the adequate additive.

The performance of the additive is essential: it strengthens the fluid bed particle for the "in situ" release of crystallization heat which evaporates the residual solution water.

This feature drastically reduces the amount of fluidization air at ambient temperature required to cool the granulator.

The multiple air nozzles with vertical upward flow attract a large amount of particles in their wake where the urea solution is injected and evenly distributed.

The geometrical pattern of the atomization nozzles just protruding through the perforated plate which supports the fluid bed, is such as to reach the highest specific capacity which can still match the heat balance of the system.

The residual cooling duty of the solid product recycle becomes negligible and the recycle ratio is only designed to balance the reseeded by crushed oversize and to stabilize the average size of the product by a reasonable fraction of fines.

The presence of formaldehyde compounds in the liquid phase of each particle creates such a cohesion force that the dust emission is kept under control to a mere 4% of product output rather than the circa 20% which could prevail without such additive.

Such a small amount of dust can be efficiently caught in standard scrubbers but lately a new environmental challenge has emerged : **ammonia emission control**.

III. Control of ammonia emission in fluid bed granulation of urea

The liquid urea feedstock to the solidification section, either as a melt or as a high-concentration solution, contains some dissolved ammonia from residual traces of ammonium carbonates, from decomposition products of urea and from dimerization to biuret.

This residual ammonia is stripped/flushed during the solidification process and is released with the cooling air into the atmosphere. The gaseous ammonia flow is then so dilute that it cannot be physically absorbed by scrubbing.

Chemical scrubbing with inorganic acids is the only well-known solution. Hydro Agri Sluiskil applies such solution in its ammonium nitrate granulation process - where the reactant is then the mainstream nitric acid.

Sulphuric acid has been proposed for urea processing, but then the resulting salts end up in the product and - if no extra separate scrubbing step is foreseen - the product is thus excluded from most technical applications.

Hydro Agri Sluiskil has therefore explored a chemical scrubbing process based on the same organic formaldehyde-based additives already used in the granulation process for product quality improvement (shape, crushing strength, anti-caking).

Gaseous formaldehyde (vaporized from a fine liquid mist injected into the hot air stream at granulator exhaust) preferentially reacts with the stripped ammonia to form HMTA (hexamethylenetetramine).

In this hot and dry atmosphere, the reaction does not suffer from competition with the standard urea-formaldehyde reaction, which would prevail in the dilute urea solution phase of the downstream scrubbing operation.

The unstable HMTA compound is dissolved in this dilute scrubbing solution which is then recycled to the vacuum reconcentration section where HMTA redecomposes to ammonia and formaldehyde. The formaldehyde is kept in solution, reacts with the large excess of urea and finally becomes a part of the granulation additive.

The ammonia is absorbed in the process water condensates and is recycled to the urea synthesis section.

Some extra precautions have to be included to control formic acid formation from entrained formaldehyde traces in the process condensates.

By this simple process Hydro Agri has been able to reduce its average ammonia emission to 0,2-0,3 kg ammonia/ton at half the unabated level of circa 0,4-0,6kg ammonia/ton, without any significant emission of the formaldehyde reactant.

At this level, a fraction of the granulation additive can still be injected via the standard route for flexibility of operation.

IV. Safety and health issues of formaldehyde-based additives

A clear distinction must be made between the additive as such and its chemical composition in the final urea product.

1. Safety and health issue of formaldehyde-based additives as such :

Formaldehyde-based raw materials are available as liquids. The formaldehyde vapour pressure above such liquids is a gas with an extremely pungent, irritating and repulsing smell.

Its smell detection limit is below ONE ppm. Its repulsion is so high that any exposed person tends to run away.

Many tests have been conducted on its health impact at levels of 8-15 ppm continuously over a complete workday with rest hours in-between, especially to evaluate carcinogenic risks.

These test conditions cannot happen in the urea applications as considered here, since human exposure is only incidental during unloading and pump switching.

By the way, formaldehyde is also an antiseptic agent which is heavily used in medical treatments without any valid alternative.

In the form of UF-pre-condensates, formaldehyde is a viscous liquid, which is not corrosive. Short contacts with the skin are painless. Its smell is the best safeguard.

2. Safety and health issues of urea treated with formaldehyde-based additives :

The formaldehyde-based additives instantaneously react with the wide excess of urea to form polymers without any residual free formaldehyde. The final product safety is not at all affected by the additive.

In the USA, the Fertilizer Institute has already clarified this in a report of February 1983.

The product can be used in all fertilizer applications, as an animal feed component and in most technical formulations, especially the urea-formaldehyde glues where the additive already replaces a fraction of the reactants.

Conclusion

Formaldehyde-based additives offer a perfect synergy with the fluid bed granulation technology of urea.

This synergy has been highly enhanced by the possibility to reduce ammonia emissions well below present levels, without extra cost and without other environmental constraints.

C - FIRST COMMERCIAL EXPERIENCE AT INCITEC Ltd

Introduction

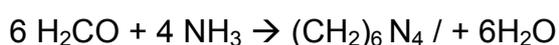
The ammonia abatement system already implemented at Hydro Agri Sluiskil in the Netherlands has also been installed at Incitec, Brisbane, Australia.

Incitec operates a urea synthesis plant with Vulcan process, for a capacity of 750 tons/day. This product was prilled. However under market pressure and environmental pressure, it was decided to switch from prill to granulation technology.

Shedden-Uhde obtained the contract for this project, which included the construction of a HFT granulation and a Stamicarbon concentration section.

Results:

One of the guarantees at Incitec was a maximum stack emission of 15 kg NH₃/h at a production rate of 740 MT/day. A guarantee that could not be achieved without an ammonia abatement system by formaldehyde, according to the reaction :



Two fine liquid pressure spray nozzles were installed through which the urea-formaldehyde (UF) was injected.

These spray nozzles were placed directly at the beginning of the outlet duct of the granulator. (present drawing)

The urea formaldehyde was diluted with water. The amount of urea-formaldehyde (UF) used for the ammonia abatement was 50% of the required urea formaldehyde to obtain up to 0.55% formaldehyde in the final product.

Method of analysis:

The first main problem we met was to agree upon the way how to measure and analyse the ammonia in the stack and the amount of free ammonia in the feedstock.

We had methods given by the Licensors, Hydro Fertilizer Technology, Stamicarbon and the Client, but also several methods from different authorities were also available.

Method for isokinetic stack flow measurements:

The method for flow measurement gave no discussions. This is a well-known isokinetic method whereby the cross section of the rectangular stack is divided into parts of equal area, having the same form as the cross section. In the selected sampling points a series of velocity pressure readings are taken with a Pitot tube. From these readings an average velocity can be calculated and so the total flow.

These measurements also allow us to calculate the sampling velocity required for the isokinetic sampling.

Method for NH₃ determination in stack flow:

The determination of the ammonia in the stack flow gives more discussions. All methods are based on the isokinetic sampling of a measured flow from the stack, but the main difference is the way that the ammonia is bound in the wash bottles of the sample system.

Three different methods were tested:

- Absorption in demineralised water (bottles in icebath)

- Chemical binding with boric acid

- Chemical binding with sulphuric acid.

The results showed a difference of more than 10% where the method with sulphuric acid gave the highest results. The discussion was mainly about the question if this result was really showing the free ammonia or also other components that where in this way analysed as ammonia.

After solving the above discussions we agreed that the method with sulphuric acid for the determination of the ammonia in the stack should be used.

Since the Incitec lab was not equipped for this method, the follow-up was done by the boric acid method. The sulphuric acid method was carried out by an external company.

Method for NH₃ Determination in urea solution:

This method was a source of a lot of discussions. This analysis is carried out by acid titration of the diluted urea solution. The discussion was mainly about the endpoint of this titration. How deep do you have to go in pH if you want to express the result in "free" ammonia?

If the pH is too low there might be some hydrolysis of the urea solution. What is the "free" ammonia in a urea solution?

For the stack emission of a granulator it is important to know the amount of ammonia that will be liberated in the granulator. This means that also the ammonia bound as ammonia carbonate will be found back as ammonia emission.

Based on the overall ammonia balance we made, we found that the analysis results by a titration to pH 4,5 gave the most reliable figures.

Measurements:

Next problem we faced was that we found out that the total NH₃ emission was far above our expectations. In a test where the ammonia abatement was not in use, we found values of more than 32 kg NH₃/h, where we expected 23 kg NH₃/h max.

The sources for NH_3 are mainly:

- 1) Ammonia formed by the reaction from urea to biuret
The increase in biuret between the melt pump and the granulator was less than 0,1%, which was according to the guarantees. This reaction gives an additional amount of free ammonia of about 5 kg to the urea solution.
Such non negligible amount was foreseen in our calculations and so part of the expected 23 kg/h.
- 2) Ammonia in the process condensate feed to the scrubber
The process condensate used as make-up water to the scrubber was expected to contain 300 ppm ammonia. Due to the design of the scrubber all this ammonia will be stripped out and will be measured as NH_3 emission. The real amount of ammonia in the process condensate was however even lower and during the tests it never exceeded the 200 ppm. This gave an additional 1.2 kg of ammonia where we expected 1.8 kg.
- 3) Free ammonia in the urea solution
The "free" ammonia in the urea solution was expected to be lower than 500ppm. All this free ammonia will be liberated in the granulator and is the main source for the ammonia emission. The only explanation for this excess of NH_3 was a higher than expected amount of free ammonia in the urea melt.
Here the expected figure was max. 500 ppm while we found values, after solving the analytical discussions, between 700 and 800 ppm.

This higher range of peculiar upstream values may be linked to the Vulcan synthesis process.

Result of ammonia abatement:

Next problem that occurred was that the first trial we carried out with the NH_3 abatement system was quite disappointing. It only gave us a reduction in NH_3 emission of 4 kg where a reduction of close to 8 kg was needed.

By checking the system in operation we found that the two UF sprayers were not covering the total surface of the outlet duct. So room for improvement was available.

We decided to improve the system by adding more sprayers. To obtain a good coverage of the surface we increased the number of sprayers from 2 to 7. Of course the size of the sprayers was reduced accordingly since the total amount of UF was not changed.

With the new sprayer configuration we did a new trial and found a reduction of about 7 kg. This result is as such not bad but left us still far away from the guaranteed figure of 15 kg NH_3 /h. The reduction was also lower than expected. For this we tried to find an explanation. By investigation at the producer of the urea-formaldehyde (UF), Borden Brisbane, we discovered that they were using a batch process with high residence time which delivers a very stable product with a high buffer capacity and a high pH.

For the ammonia abatement it is important to have enough free formaldehyde. This is the component that is directly reacting with the ammonia. A too stable urea-formaldehyde (UF) could explain a lack of reaction component.

Tests in laboratory prove that the urea-formaldehyde (UF) produced according to the mentioned process is much more stable than the urea-formaldehyde produced according to a continuous direct absorption process.

It is an excellent product for most applications, however not in favour of ammonia abatement.

To meet our guarantee on ammonia emission there were only two things left.

- 1) Reduction of the free ammonia in the urea solution
 This was of course the most favourable solution. A lot of trials in close co-operation with Stamicarbon were carried out. By changing process parameters like vacuum and temperature in the pre- and final-evaporator we tried to reduce the free ammonia in the urea solution.
 However this did not give us the desired result. Also changing the water content in the feed to the final evaporator did not reduce the free ammonia in the urea solution.

- 2) The use of formaldehyde instead of urea-formaldehyde
 To prove the theory that the free formaldehyde is the reaction component we agreed to carry out a test with formaldehyde instead of urea-formaldehyde.
 Borden has 37/1 as intermediate product. This is a water solution containing 37% formaldehyde and maximum 1 % methanol. Here all the formaldehyde is present as free formaldehyde. The product was delivered in 1000 litre containers, which we connected directly to the suction of the formaldehyde pumps.
 Since the temporarily suction line gave a high pressure drop and the 37/1 is containing 37% formaldehyde where the urea-formaldehyde contains 55% we had to run with two pumps in parallel.
 The results of the test with formaldehyde 37/1 showed that it was possible to reduce the total ammonia emission by almost 50%. During the test the emission was reduced from 31.2 kg/h to 16.3 kg NH₃/h.

Impact of the ammonia abatement system on the process

The reaction time of the overall system is low. The hexamethylene tetramine is dissolved in the scrubber solution. Due to the huge volume of the scrubber it takes a long time before we can reduce the direct injection of urea-formaldehyde (UF) in the urea solution.

At Incitec it took more than 24 hours before we saw an increase of the formaldehyde content in the final product.

We should however mention that due to the fact that there was only one scrubber, this effect was amplified. In installations with a higher capacity, there are normally two scrubbers installed and the volume of the granulator scrubber per ton of product is much lower.

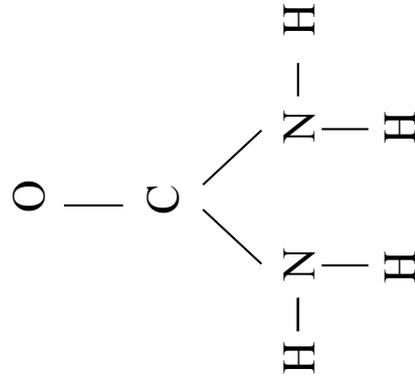
Due to the injection of urea-formaldehyde (UF) in the line to the scrubber, we saw a very fast build up of product in this line. This was increasing the pressure drop, resulting in the opening of the suction valve of the exhaust fan.

Only by spraying water via the saturation sprayer installed just before the urea-formaldehyde sprayers we kept the line open.

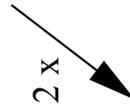
By continuously adding the make-up water of the scrubber via this sprayer, we overcame this problem without affecting the efficiency of the ammonia abatement.

Conclusions:

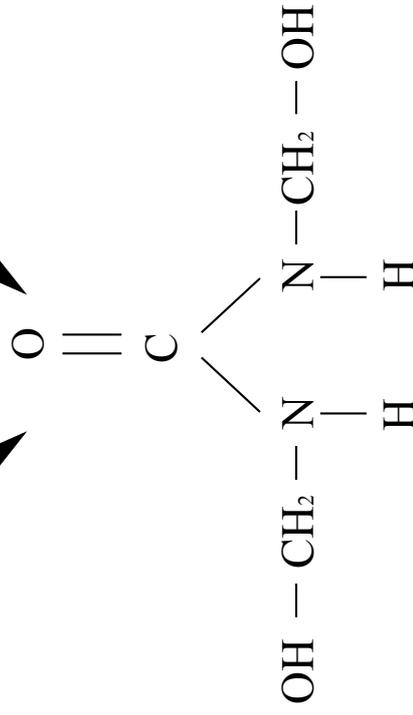
- The results obtained show that it is possible to reduce the ammonia emission by using the ammonia abatement system based on urea-formaldehyde (UF).
- The system is sensitive to the type of urea-formaldehyde (UF). Free formaldehyde is the active component. If not easily available due to a too stable molecular structure, the efficiency will be lower. The maximum possible efficiency we found was a reaction of 40% of the free formaldehyde.
- The ammonia abatement system is cost free. All the ammonia reacted with formaldehyde to hexamethylene tetramine is recycled to the pre-evaporator where it decomposes again to formaldehyde and ammonia. The formaldehyde is then used as the standard urea additive.
- Methods of analysis should be discussed among parties and confronted with those of the actual plant site and the external surveyor prior to final process design.

UREA

1 x

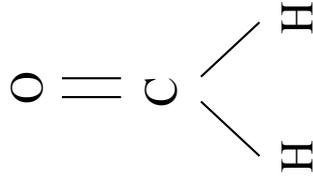


2 x

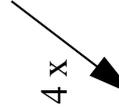


DIMETHYLOLUREA

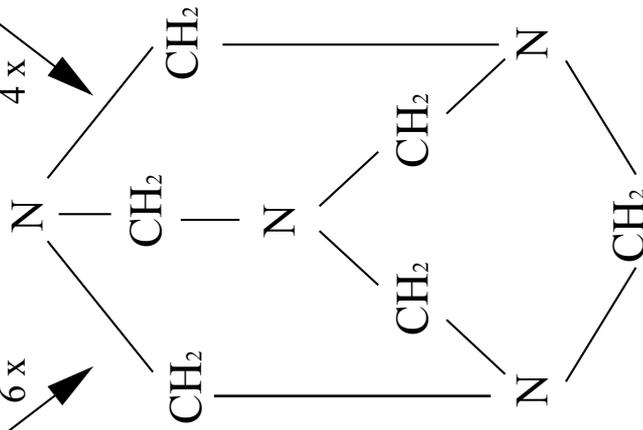
(among others)

FORMALDEHYDE

6 x



4 x



HEXAMETHYLENETETRAMINE

(and water)

AMMONIA