Stamicarbon bv

Has emission abatement a pay back time ?

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1. PREFACE

Stamicarbon has been established 1947, and is the wholly owned licensing subsidiary of the Dutch chemicals producer DSM. Stamicarbon licenses proprietary processes, know-how and expertise, developed and commercially proven by its mother company.

The chemical group DSM NV is a private corporation with its main offices in the Netherlands. DSM is on global basis active in several areas of the chemical process industry, and has about 22.700 employees world-wide.

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2. INTRODUCTION

In every continent of our world environmental pollution in general and air and water pollution especially are becoming an ever increasing concern. Governmental regulations become more and more strict.

A pro active approach of the fertiliser industry can avoid major conflicts and can even turn these restrictions into opportunities, which can save a considerable amount of money.

This paper will discuss in detail three areas in which emission abatement projects go hand in hand with a certain profitability.

The first area is the reduction of gaseous ammonia emissions from absorbers and the losses of valuable feed stock mainly in urea plants which operate at higher capacity than their original design capacity. Several examples will show their profitability.

The second example is the reuse of waste water in a urea plant as boiler feed water for the production of steam. This example will be illustrated with practical experience and will discuss important attention points mainly related to the application of formaldehyde.

The third example is emission abatement from prilling towers and granulators.

Finally a summary with conclusions will be presented.

3. EMISSIONS IN UREA PLANTS

Every urea plant has a certain amount of gaseous emission into the atmosphere and a certain amount of liquid emission into a sewer system. These emissions can be split up by continuous and discontinuous emissions.

Important continuous emission points are:

- NH_3 gaseous emission from the high pressure scrubber or from the medium pressure (operating at 7 or 4 bars) absorber located downstream the high pressure scrubber.
- NH_3 gaseous emission from the atmospheric absorber or low pressure scrubber located downstream the low pressure carbamate condenser
- NH_3 gaseous emissions from the prilling tower or the granulator
- NH_3 gaseous emissions from the stack from e.g. leaking safety valves
- NH_3 gaseous emissions from various spindles, flanges, etc.
- NH_3 and urea liquid emissions from the desorption section
- Urea dust emissions from the prilling tower or the granulator

Important discontinuous emissions can occur during start up, shut down, failure of e.g. power or cooling water and blowing off of safety valves

Stamicarbon has developed techniques and/or procedures to reduce all process related emissions.

4. THE ECONOMICS AROUND EMISSION ABATEMENT

Many times emission abatement projects are triggered by ever tightening environmental regulations. On the other side of the coin however the reduction of losses of valuable feed stock and/or reusing waste streams can contribute to the profitability of these projects.

This paper will discuss in detail three areas/examples in which emission abatement projects go hand in hand with a certain profitability.

4.1. Absorbers

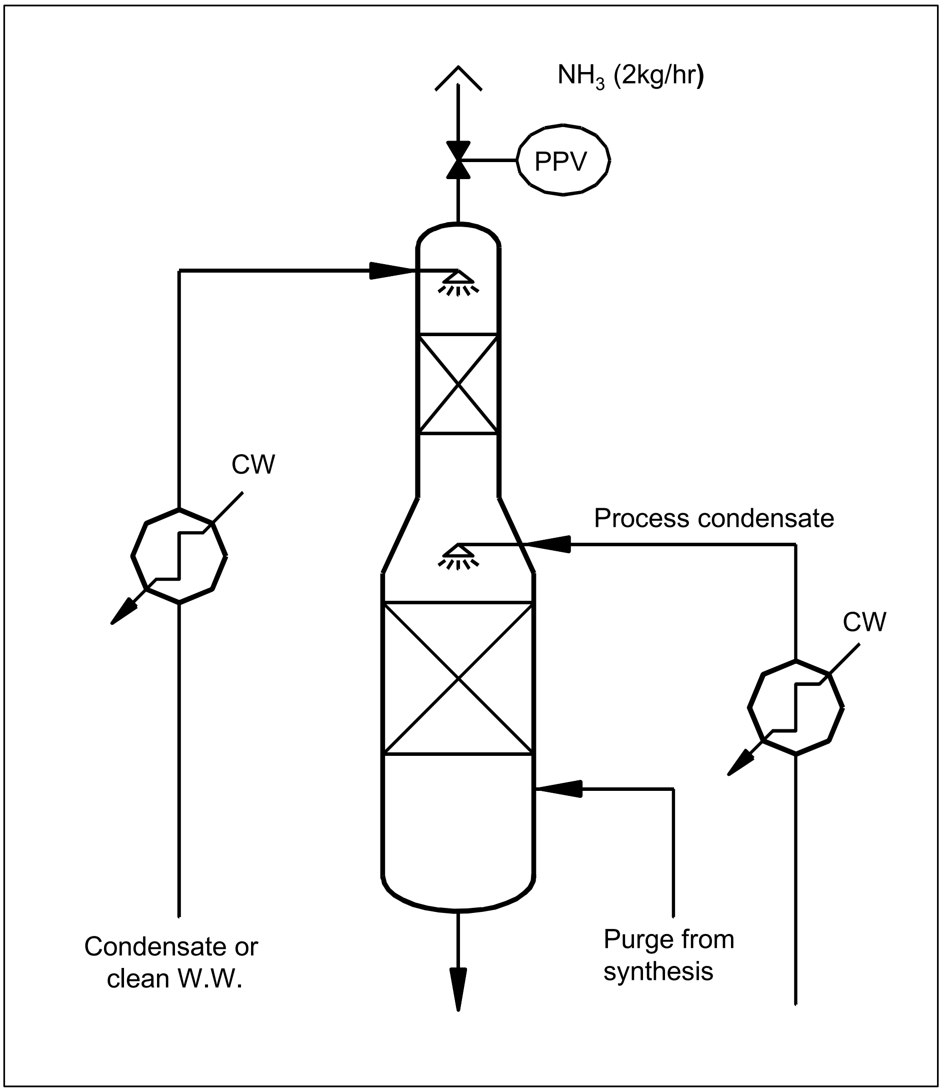
After the first start up of a urea plant and after the initial operating period the operators learn to operate the process better and many urea plants operate at higher loads than the original design capacity. This higher capacity can be achieved by using the margins in the design originally meant for summer conditions, fouling, etc.
These plants produce more urea, sometimes even up to 125% of the original design capacity, and accept often extra ammonia losses from, for example, the absorbers at these higher loads.

Ammonia emissions increase sometimes from the design values in the order of 1 to 5 kg/hr to values of 500 to even 1000 kg/hr representing some 100 US$/hr.
These high ammonia emissions can be reduced again to design levels by installing additional coolers in the wash water flows to the absorbers, by installing a bigger absorber and/or installing more condensing capacity in the vacuum condensers in this way reducing the ammonia flow to the absorber. These process equipment items are all low pressure equipment items, so investment costs are limited.

Taking into account that a ton of ammonia is normally worth at least 100 US$, one can easily see that saving this amount of feed stock pays back very quickly. Several examples show that these kind of projects lead to short pay back times like 1 to 2 years.

For example a Stamicarbon stripping plant with an original design capacity of 1600 mtpd designed in the 1980's, operates at an actual capacity of nearly 2000 mtpd by using the design margins available. This plant did not yet have a 4 bar absorber downstream the high pressure scrubber. At the higher load the ammonia emission from the scrubber was between 250 and 400 kg/hr. Assuming an ammonia price of 100 US$/mt this means a yearly loss of about 300.000 US$.

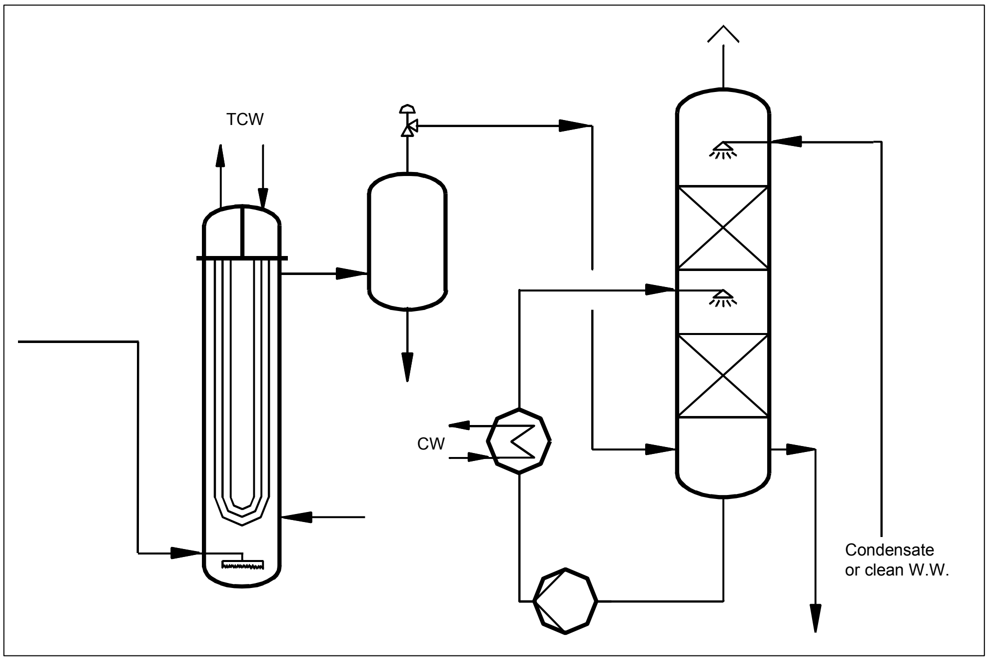
Figure 1: A typical modern 4 bar absorber system



The total investment for a new 4 bar absorber system as indicated in Figure 1, which reduces the ammonia emission to less than 2 kg/hr, is estimated to be about 500.000 US$ based on European conditions. This means that this project had a pay back time of less than 2 years, again based on European conditions.

Another example is the ammonia emission from the low pressure scrubber. In many older plants the low pressure scrubber has an open connection to the level tank of the low pressure carbamate condenser. At higher plant loads the ammonia emission from the low pressure scrubber may exceed 100 kg/hr. By disconnecting the low pressure scrubber from the level tank and installing an atmospheric absorber the ammonia emission can be reduced to less than 5 kg/hr.

Figure 2 shows the situation of the low pressure carbamate condenser and an atmospheric absorber.



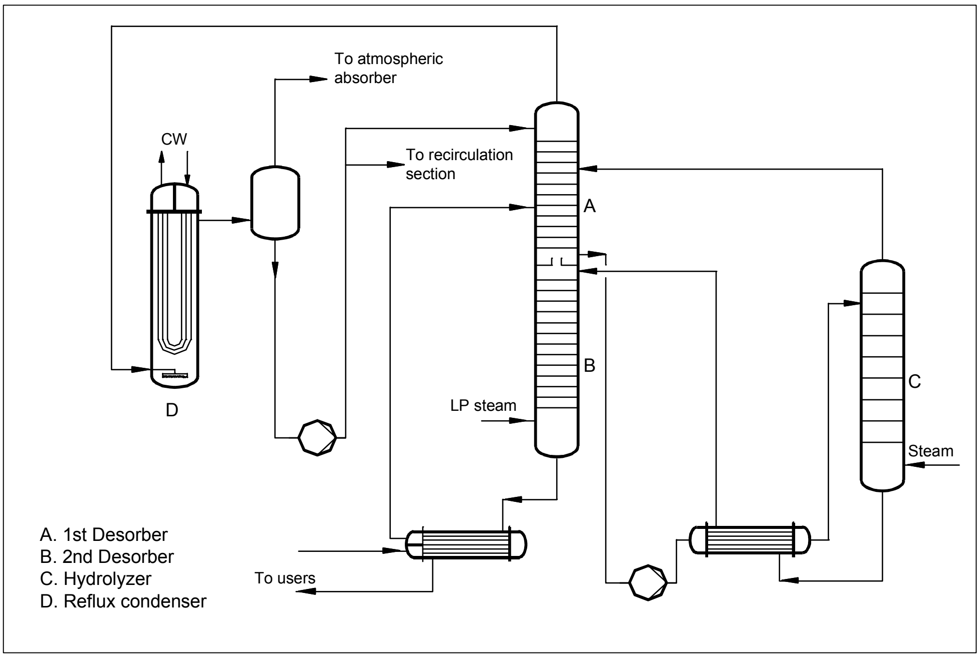
The estimated equipment investment for this modification in a 1500 mtpd urea plant is about 100.000 US$. In Europe this would mean a total investment of about 350.000 US$. The annual saving is between 100 and 200 kg/hr ammonia or about 180.000 US$ assuming an ammonia price of 100 US$/mt. These assumptions lead to a pay back time of less than 2 years.

4.2. Modern waste water treatment

A urea plant produces water as well as urea. This water, which is contaminated, mainly by entrainment from the evaporation section, requires treatment if it is to be reused again. It is of course obvious that avoiding contamination is more economic than treatment of this process water. Stamicarbon can give a number of advises how to minimize the contamination.

A modern Stamicarbon waste water treatment reaches sufficient low levels of ammonia and urea to reuse purified process condensate as boiler feed water for the production of steam as has been proven in many plants during many years already. This chapter discusses the important issues to consider. Figure 3 shows a process scheme of a typical modern Stamicarbon waste water treatment.

Figure 3 : Process Water Treatment System



Typical features

A modern Stamicarbon waste water treatment consists mainly out of a first desorber column, which reduces the ammonia content. At the same time carbon dioxide, which is much easier to desorb, will be reduced. This column operates at a low pressure which facilitates the desorption process.
For the next column, the hydrolyser, it is important that the ammonia concentration at the inlet is sufficiently low, in this column retention time is required whilst at the same time the ammonia and carbon dioxide in the liquid phase must remain sufficiently low in order not to reach the chemical equilibrium. Under these conditions the hydrolisation reaction proceeds towards the ammonia and carbondioxide side, reducing the urea content to virtually zero.

$$UREA + H_2O <==> 2\,NH_3 + CO_2$$

Contrary to other commercial hydrolysers, our hydrolyser is operated as a counter current bubble column to improve the efficiency; water with urea meets continuously relatively clean vapours during its way through the column from the top to the bottom.

In the hydrolyser the ammonia and carbon dioxide content in the liquid will rise due to the above mentioned reaction. Also contrary to other hydrolysers the Stamicarbon hydrolyser is operated at relatively low pressures (20 bar) resulting in a temperature of about 200°C causing the equilibrium reaction to proceed sufficiently fast.
At the outlet of the hydrolyser the urea content is decreased to ppm level.
The temperature in the hydrolyser is maintained by the injection of 20 bar steam.

In the second desorber column again operating at low pressure the ammonia and carbon dioxide content are also decreased to ppm level. The stripping in the second desorber is done by using life low pressure steam injected in the bottom.

Vapours from the hydrolyser and second desorber are used for the stripping in the first desorber. Nowadays the first and second desorber are integrated into one sieve tray column to save investment costs.

The vapours of the first desorber, which contain ammonia, carbon dioxide and water are condensed in a submerged reflux condenser and form a carbamate solution.
A reflux condenser disconnects the waste water treatment section from the recirculation section leading to considerable more operating flexibility.
With help of a reflux stream the water content in the off gases of the first desorber and thus in the carbamate can be controlled.

A submerged type condenser reduces the influence of pressure variations and leads to a stable and easy operation. This will assure a constant quality of the waste water or better purified process condensate.

Two process-process heat exchangers decrease the needed high pressure (20 bar) and low pressure steam amounts considerably.

Due to the mild process conditions corrosion problems have not been encountered with this hydrolyser system.

This modern Stamicarbon waste water treatment system is well proven, it has been applied in more than sixty units for upto than 15 years. The capacity of these units vary between 10 and 80 m3/hr waste water. Several units operate as stand alone units cleaning the waste water from several different urea plants or lines.

Typical consumption figures for a modern Stamicarbon waste water treatment in a urea plant with a two stage evaporation upstream a prilling tower are:
- 250 kg low pressure steam per cubic meter waste water
- 65 kg high pressure (20 bar) steam per cubic meter waste water
- 15 ton cooling water per cubic meter waste water
- power consumption is negligible

Concluding: The design of a modern Stamicarbon waste water treatment has been optimized between three important criteria being investment costs, operational costs and reliability.

Formaldehyde in the process water

Formaldehyde in the feed to the waste water treatment section originates mainly from the application of a formaldehyde solution to improve the crushing strength and caking tendency of the prills or granules. There are several types of formaldehyde solutions available on the market for example urea-formaldehyde solutions, HMT and formaline.
The use of UF85 Formaline on granulation scrubbers, to reduce the emissions could, via the recycle line to the front-end of the plant, be another source of formaldehyde in the feed to the waste water treatment section.

Formaldehyde may decompose to formic acid at the hydroliser temperature since formaldehyde can react with itself resulting in formic acid and methanol.

Traces of oxidizing components e.g. oxygen react with formaldehyde to formic acid.

It is known that dosing a UF85 formaline solution to the urea solution tank to improve the quality of prills will lead to formic acid in the outlet of the waste water treatment section. In the evaporation section formaldehyde will entrain together with the vapours, condense in the vacuum condensers and enter the ammonia water tank. In the hydrolyser formaldehyde will decompose to formic acid according the earlier mentioned reaction.

Formic acid might increase the corrosivity of the waste water, increases the conductivity and reacts with ammonia according the following reaction:

NH_3 + H+ + HCOO- --> NH_4+ + HCOO-

This means that dosing formaldehyde increases also the ammonia content in the purified process condensate.

One way to avoid these problems is to relocate the UF85 dosing from the urea solution to the urea melt after the evaporation section. If one doses in the suction of the urea melt pump the melt pump will provide the required mixing.

A disadvantage in a urea plant with a prilling tower is that the melt and possibly also the prills will contain a higher moisture content. Some clients accept this disadvantage.

There is a feasible solution to handle this problem; installing a mixed bed ion exchanger to absorb the formic acid. Several ion bed exchanger manufacturers have confirmed that it is very well possible to absorb formic acid.

Actual experience

If one would ask a turbine or boiler manufacturer the minimum requirements of the quality of the boiler feed water, he will answer that among others the ammonia and urea content should be below 0.1 ppm.
It is clear that the cleaner the boiler feed water, fewer risks for the turbines and boilers are taken. On the other hand these guidelines are based on power plants and no scientific basis is available for these very strict requirement.

It is also clear that the production of high pressure steam will require more strict quality figures for BFW than the production of low pressure steam as the temperature and the risk of corrosion will be higher.

An investigation of the actual experiences of several clients who use the purified process condensate as boiler feed water lead to the following overview:

Many Stamicarbon clients use the waste water or purified process condensate as cooling water make up. This is a good alternative in case cooling towers are applied. However when sea coolers or air coolers are applied the amount of cooling water make up required is only a relatively small amount.

Reusing the purified process condensate as boiler feed water is always a more attractive option.

- Several clients operate a urea plant with a prilling tower without dosing a formaldehyde solution. Since 1987 40 bar steam is produced directly from purified process condensate without any conditioners.
- Another client operates a urea plant with a prilling tower without dosing a formaldehyde solution. Since 1994 purified process condensate is used via a standard polishing unit to produce 125 bar steam.
- One more client operates a urea plant with a Hydro Fertiliser granulation section without dosing a formaldehyde solution to the scrubbers of that granulation. Since 1997 50 bar steam is produced from purified process water after treatment of this water in a standard polishing unit.
- Two more clients operate urea plants with a Hydro Fertiliser granulation unit without dosing a formaldehyde solution to the scrubbers. Since 1993/4 they produce low pressure steam from purified process water directly in the high pressure carbamate condenser.
- A last client operates a urea plant with a Hydro Fertiliser granulation section and doses a formaldehyde solution to the scrubber. Since early 2000 this client produces 40 bar steam via a polishing unit including a mixed bed ion exchanger.

Conclusions

1. Several clients prove that without dosing a formaldehyde solution to the urea plant the reuse of purified process condensate as boiler feed water for steam with a pressure up to 40 bar is possible without further treatment of the outlet of the second desorber.
2. Several clients prove also that with dosing a formaldehyde solution to the urea plant the reuse of purified process condensate as boiler feed water for low pressure steam (up to 6 bars) is possible without further treatment of the outlet of the second desorber.
3. Urea plants re-using the purified process condensate as boiler feed water for the production of high pressure steam (higher than 40 bars) treat the outlet of the second desorber first in a standard polishing unit.
4. When a formaldehyde solution is applied in the dust scrubber to reduce the ammonia content a mixed bed ion exchanger may avoid any contamination of the purified process condensate.

It is possible to transform an old design waste water treatment into a modern Stamicarbon waste water treatment. The existing co-current hydrolyser needs to be changed into a counter current hydrolyser, which requires changing the pipelines around the hydrolyser and a modification of the trays. The existing desorbers need more trays, which can be accomplished by increasing the height of the desorbers. The diameter will be sufficient and does not require changing.

In a 1500 mtpd urea plant the total investment costs based on European conditions would amount to about 2-2.5 million US$.
In some area's boiler feed water is valued up to 3 US$/m3 leading to a yearly saving of 35 m3/hr demi water or about 900.000 US$. This leads to a pay out time of less than 3 years not even considering the savings in urea and ammonia otherwise lost.

4.3. Emissions from prilling towers and granulators

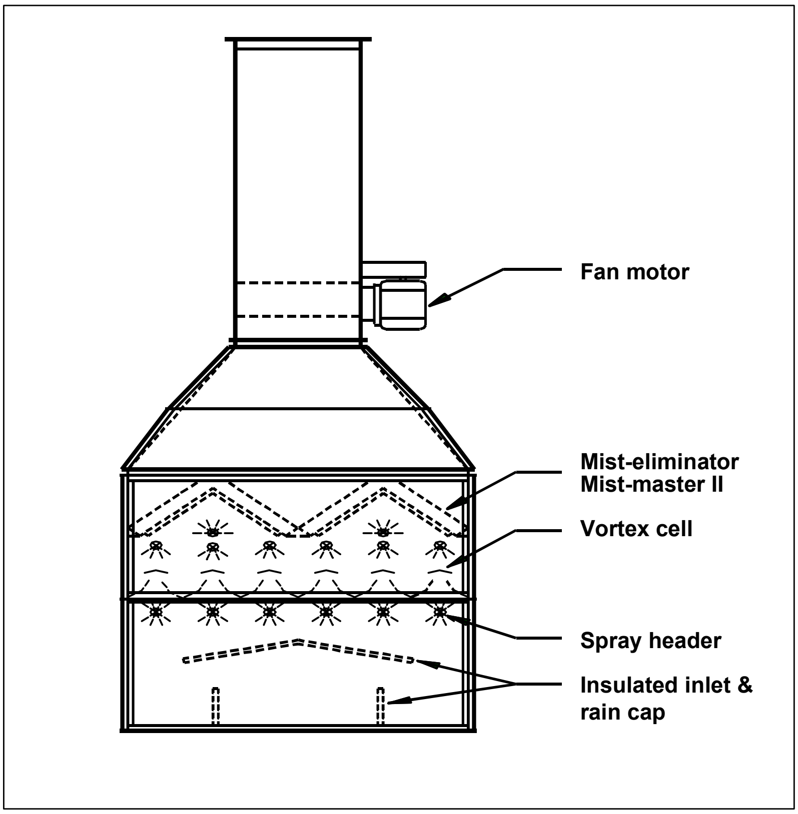
Governmental regulations for the emissions of prilling towers and scrubbers of granulators become more and more strict. Allowable emission levels are currently maximum 50 mg/Nm3 dust and 50 mg/Nm3 ammonia.
Not meeting these requirements might lead to forced plant closure.

Prill tower

The dust emission from a prilling tower can be very effectively reduced by a scrubber system. In the past Stamicarbon evaluated different techniques of dust scrubber systems and concluded that the dust scrubber of BECO Engineering Company from the USA is a good option.

The wet scrubbing technique of BECO applies two mechanisms to remove urea dust particles from a prill tower exhaust air stream: particle agglomeration and separation.
Figure 4 for provides an overview of a BECO dust scrubber.

Figure 4: Overview of a BECO dust scrubber.



Air leaving the prill tower is hot and dry, while urea is hygroscopic. The relative humidity must be raised to the point where collected urea dust will absorb moisture and tend to liquefy.

The provision for agglomeration is comprised of a series of vertical-flow vortex cells. The cells converge air flow against and around a transverse baffle, forming stabilized gas vortices on the downstream side of the baffle.

Recycle urea solution is injected as a fine spray into both the approach section and the downstream vortices, resulting in efficient humidification and particle drop agglomeration.
The efficiency of the separation step is the key to the performance of the scrubber. In BECO scrubbers, the separator is comprised of a patented high-efficiency, high-capacity mist eliminator, the BECO " Mist-Master II". This single-stage mist eliminator is capable of removing all particulates and droplets down to 0.7 microns in size.

Scrubbers can be located either on grade, or preferentially, on the prill tower roof to avoid long, large and thus expensive ducts. The location is determined largely by structural integrity of the prill tower; most BECO installations have been located on the prill tower roofs.

The pressure drop across the scrubber is in the order of 60 mm WC. Both the scrubber pressure drop and the tower air flow are provided by the scrubber exhaust fans, placed in the exhaust stacks of the scrubbers.
Additionally ammonia emission can be reduced in a BECO scrubber by washing with nitric or sulfuric acid. This will lead to urea-ammonium nitrate or urea-ammonium sulfate solutions which can be sold locally as liquid fertiliser.
Another option is to use a formaldehyde solution spray ahead of the scrubber to form hexamethylene tetramine. This option allows the return of the blowdown solution to the process, but is inherently limited with respect to the degree of ammonia removal it can offer.

Ammonia and dust emission figures of about 10 mg/Nm3 have been realised, which fulfills easily the usually applied environmental regulation.
An indicative figure for the total installed investment cost for a BECO dust scrubber for a 2000 mtpd forced draft prill tower reducing the dust emission from 140 mg/Nm3 to max 50 mg/Nm3 would be between 2 and 3 million US$ depending on local installation costs.
The estimated total weight will be about 170 tons.
The indicative power consumption figure would be about 600 kW for a prill tower with an airflow of about 600.000 Nm3/hr.

Table 1 shows the reference list for urea prill tower installations

Company	Location	air flow [Nm3/hr]
Atlas Powder	Joplin, Missouri	60,000
Borden Chemical	Geismar, Louisiana	350,000
Chemie Linz	Linz, Austria	425,000
Enichem	Ferrara, Italy	45,000
ICI	Billingham, England	135,000
Ruwais Fertilizer	Abu-Dhabi, UAE	500,000
SPIC Fertilizers and Chemicals	Jebel Ali,UAE	500,000
SOIDC	Iraq	725,000
Taiwan Fertilizer	Miaoli Plant, Taiwan ROC	450,000
Terra International	Sioux City, USA	100,000
Zaklady Azotowe Pulawy	Pulawy, Poland	1,200,000

Granulation

In Hydro Fertiliser granulations exhaust air with urea dust is also washed in a wet scrubber. In granulators the dust particles are more coarse and thus easier to catch. Normally wetted mist eliminators are sufficient to reach accepted dust emission figures.

The standard scrubbers in a Hydro Fertiliser granulation achieve already a urea dust emission of less than 30 mg/Nm3, sometimes even 10 mg/Nm3.

The normal ammonia emission from these scrubbers is in fact the free ammonia in the urea melt fed to the granulator. Hydro Agri claims that this figure can be reduced with about 50-60% if an injection of a UF85 solution to the scrubber is applied. The effect of the injection of the formaldehyde solution, which will be returned as scrubber blow down to the urea plant, has been described in Chapter 4.2.

5. CONCLUSIONS

The reduction of the emissions of a urea plant will become increasingly important everywhere in the world.

In many cases the reduction of these emissions leads to economically viable projects, not only protecting the environment but also improving the plant performance, projects for optimalisation of absorbers and in the waste water treatment section are of this category. Projects to reduce dust and/or ammonia emissions from a prill tower or a granulation are merely environmental projects and cannot be justified in a direct economic calculation. These investments however will certainly please the plant neighbours.

The re-use of purified waste water can be economically viable, whereby the profitability of a purification project depends to a large extend on the availability of raw water and the costs of BFW in the fertilizer complex.

Stamicarbon has the expertise and experience to assist in the realisation of projects, improving the urea plant performance environmentally in combination with sound economics.

We would like to thank BECO and Hydro Fertilisers for their constructive co-operation in preparing this paper.