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# PUGMILL GRANULATION: A STATE OF THE ART PROCESS FOR CAN AND OTHER AMMONIUM NITRATE BASED FERTILISERS (a)

Harald Franzrahe and Paul Niehues\*, Uhde GmbH, Dortmund, Germany

## 1. Abstract

Pugmill granulation, just like the prilling process, was once one of the mainstays of the fertiliser industry. Today many other granulation processes are available which may have or claim to have certain advantages over the 'old' granulation process.

But just like the prilling process, which still has its place in the industry, a modern pugmill granulation plant also has characteristics, which make it attractive for certain applications.

In this paper we will outline the developments carried out to improve the pugmill process making it a viable option for the modern fertiliser industry.

*Uhde's technology is based on over 50 years of experience in the designing of neutralisation and granulation plants. This technology is continually being reviewed to keep abreast of current developments in equipment, materials, environmental and safety requirements, as well as trends in the marketing and application of nitrogen fertilisers.*

## 2. Introduction

### 2.1 Basic Chemistry of CAN Manufacture

Ammonium nitrate and calcium ammonium nitrate fertilisers are produced from ammonium nitrate, which is mixed with filler. To this filler other additives can be added to supply the minor elements to produce the required fertiliser grade.

It is a two-step process; first the melt is mixed with the required filler and/or additives and then granulated.

For the production of calcium ammonium nitrate or ammonium nitrate fertilisers dolomite or limestone is usually used as filler material. This is because calcium carbonate and magnesium carbonate reduce the rate of decomposition of ammonium nitrate. This improves the safety of the production process and the stability of the fertilisers during storage and transport.

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\* Head of Process Department, Fertiliser Division  
Address: Krupp Uhde GmbH  
Friedrich Uhde Straße 15  
44141 Dortmund, Germany

Phone: +49 231 547 2963  
Fax: +49 231 547 3335  
E-mail: [NiehuesP@kud.thyssenkrupp.com](mailto:NiehuesP@kud.thyssenkrupp.com)

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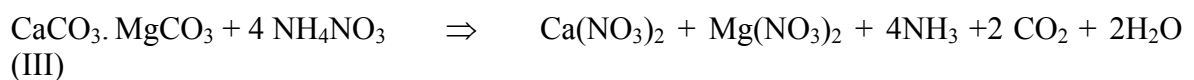
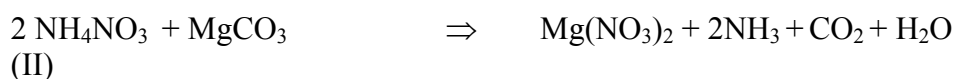
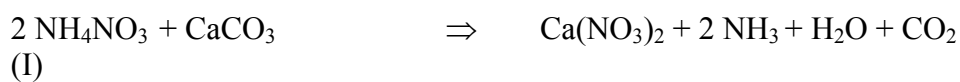
Dolomite is a naturally occurring mixture of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . Limestone can be from natural sources or synthetic  $\text{CaCO}_3$  from a nitrophosphate plant. Natural limestone and dolomite ores can be broadly classified as shown in the following table.

Type	MgO Content Wt. %	Ca Mg(CO <sub>3</sub> ) <sub>2</sub> content Wt. %
Limestone	0 – 1,5	0 – 7
Dolomitic limestone I	1,5 – 5,5	7 – 25
Dolomitic Limestone II	5,5 – 11,0	25 – 50
Limestonic Dolomite I	11,0 - 16,5	50- 75
Limestonic Dolomite II	16,5 – 20,5	75 – 95
Dolomite	0,5 – 21,8	95 - 100

Some other additives, which can be added, are:

Compound	Formula	Use
Iron sulphate	$\text{FeSO}_4$	Granulation aid, micronutrients
Aluminium sulphate	$\text{Al}_2(\text{SO}_4)_3$	Granulation aid, stabiliser
Gypsum	$\text{CaSO}_4$	S Fertiliser
Ammonium sulphate	$\text{NH}_4(\text{SO}_4)_2$	S Fertiliser
Epsom salt	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	micronutrients
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	micronutrients

The main chemical reactions occurring during the granulation process are :



All reactions can only occur if water is present, e.g. dissolution of ammonium nitrate

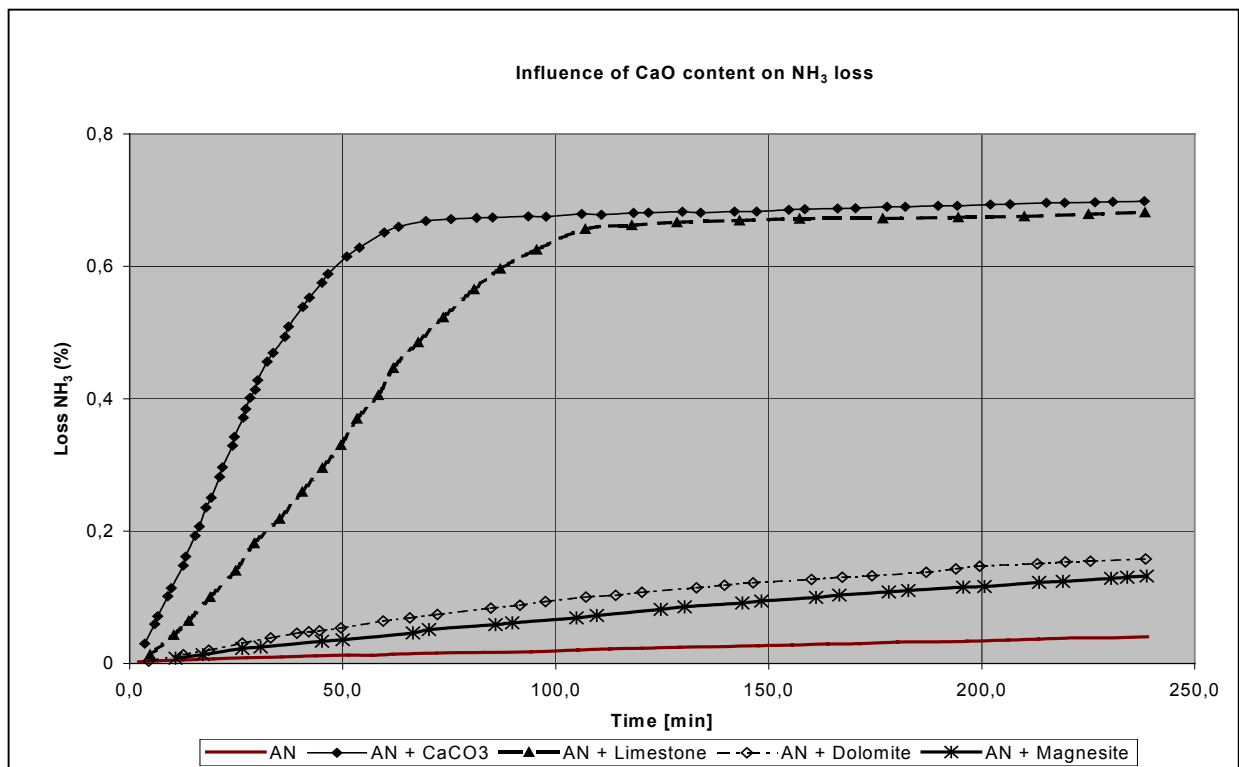


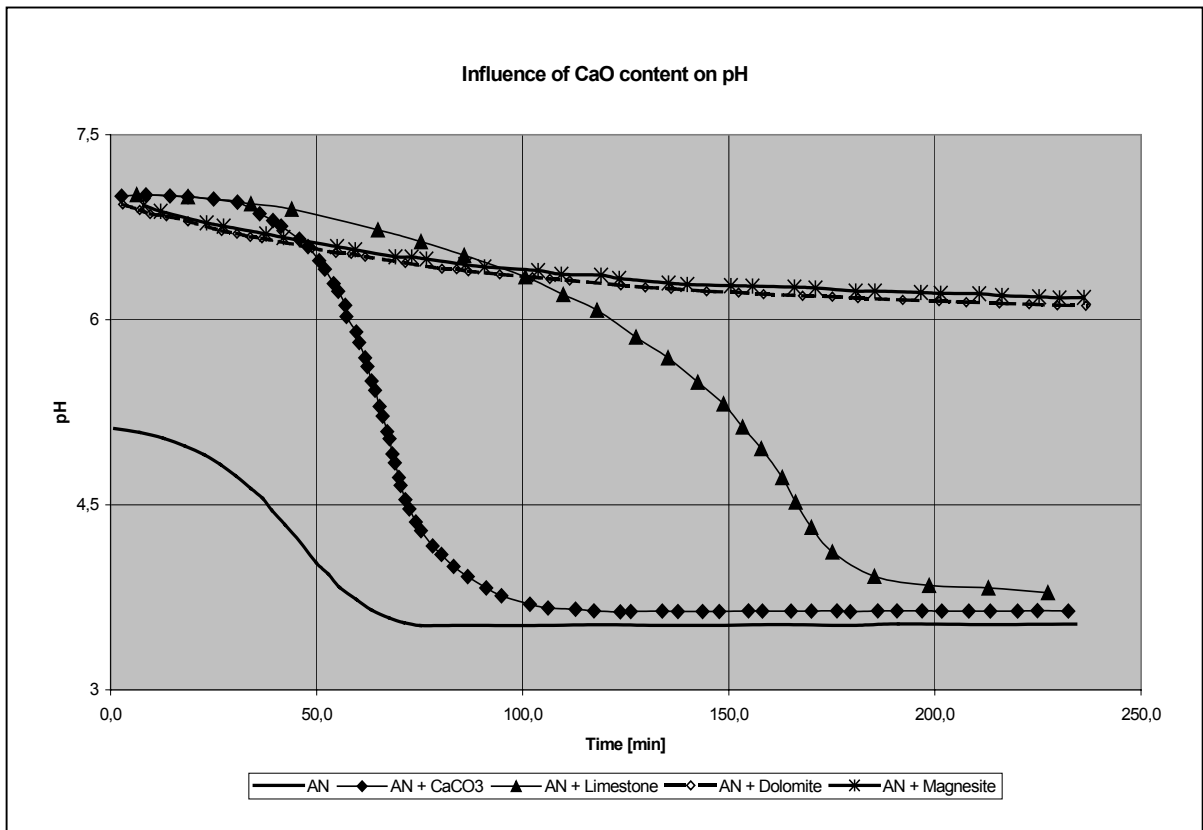
The reactivity is a measure of the intensity of the reactions between ammonium nitrate and the carbonate compounds of the filler. It is expressed as the total weight percent of nitrate in the form of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  in the granules. A high reactivity means that more  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  are formed according to reactions (I) and (II).

In general, the reactivity of a filler decreases with the CaO content of the filler - with pure  $\text{CaCO}_3$  having the highest, followed by limestone, then dolomite and ending with magnesite, which has the lowest reactivity.

This is demonstrated in the following two diagrams. They show the percentile mass loss of  $\text{NH}_3$  from a mixture of ammonium nitrate and different fillers at  $160^\circ\text{C}$ . At this temperature the conversion reactions described above occur and gaseous  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are released. Due to the good reactivity pure  $\text{CaCO}_3$  exhibits the quickest and highest release of  $\text{NH}_3$ , even higher than for pure ammonium nitrate. The addition of a filler containing dolomitic carbonate reduces the  $\text{NH}_3$  loss significantly with the lowest mass loss occurring with the addition of magnesite.

The  $\text{NH}_3$  loss results in a drop in the pH of the sample, which is shown in the second diagram. The most pronounced drop occurs in pure ammonium nitrate. Again the drop in pH is reduced by adding fillers with a dolomitic carbonate component. This stabilising effect reduces decomposition reactions of ammonium nitrate. This is why calcium ammonium nitrate fertilisers with an N content of below 28% are considered safe and exempt from many of the strict regulations pertaining to AN containing fertilisers in the EU.





The rate of reaction can be influenced by:

- pH of granules
- filler type
- drying and grinding conditions for the filler
- granulation temperature
- granulation moisture
- product moisture

While a certain amount of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  improves granulation conditions by helping to form hard and round granules, a high content leads to products with a low critical humidity and a tendency to cake in storage. If the reactivity of the filler is too high then the rate of reaction must be limited. This can be done by changing the pH, the residence time or by blending fillers with high and low reactivity.

In most pugmill plants the ammonium nitrate melt and the filler are added directly to the granulator. This gives the plant a relatively short and fixed residence time, i.e. the time period between initial mixing and crystallisation in the granulator. With this system the residence time can only be optimised for one combination of product grade and filler. Adapting to changes in reactivity is difficult and this limits the plants to staying close to the original design specifications for filler and products.

In order to achieve a better process control a mixing device has been developed. This makes it possible to increase or decrease the residence time of AN melt and filler prior to feeding it to

the granulator. This gives the plant the possibility of adapting to changing filler reactivity (e.g. when using a different filler) or different products. A device of this design was installed in a granulation plant and trials were conducted during AN production.

The device has proved to be very successful, enabling the plant to change from one type of filler to a totally different type without any noticeable change or upset in process conditions. The granulation improved considerably, allowing the plant to manipulate the product size simply by changing the recycle ratio.

## **2.2 Ammonium Nitrate Granulation Processes**

Prilling used to be the favoured process to produce AN fertilisers. However, prilling has largely been superseded by the granulation processes which nowadays produce the majority of AN and CAN products. In fact, many prilling plants have been replaced by granulation units, mainly because of environmental problems of the prilling towers but also due to the superior product quality (hardness, size, storage properties) of the granules. Currently the only market where prilling plants are still being built is that for technical and explosive grade AN.

### **2.2.1 Common AN Granulation Processes**

The granulation processes can be divided into high recycle processes e.g.

- Pugmill
- Spherodizer
- Drum

and low recycle processes

- Fluid bed
- Pan
- Fluidised Drum

Recycle in this case is defined as the amount of material going back to the granulator in relation to the amount of product being produced. A high recycle process will have a recycle of 1.5 - 2, whereas a low recycle process will usually stay below 1.

These differences result in the different AN concentrations or amount of liquid phase required by the granulation process. A high recycle granulation process usually requires a lower AN concentration (94 - 96.5%) than a low recycle process (98 - 99.5%). This correspondingly means that the amount of water, which must be removed from the product by drying, is higher for high recycle process. Some low recycle processes operate with such low water contents so that a dryer is not required.

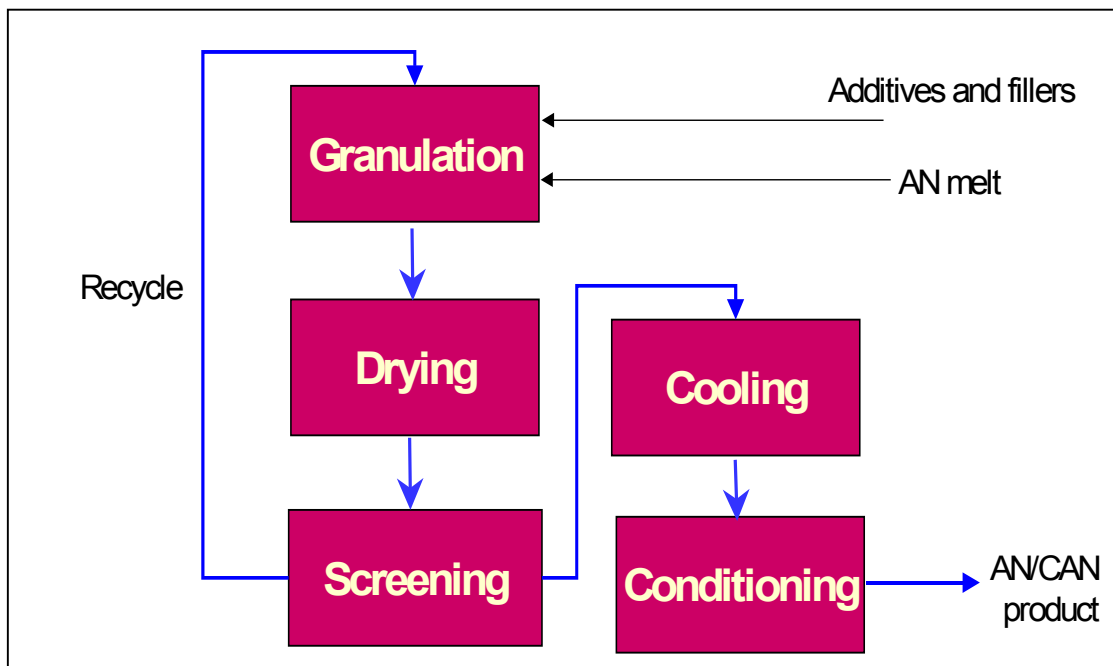


Figure 1: Granulation block diagram

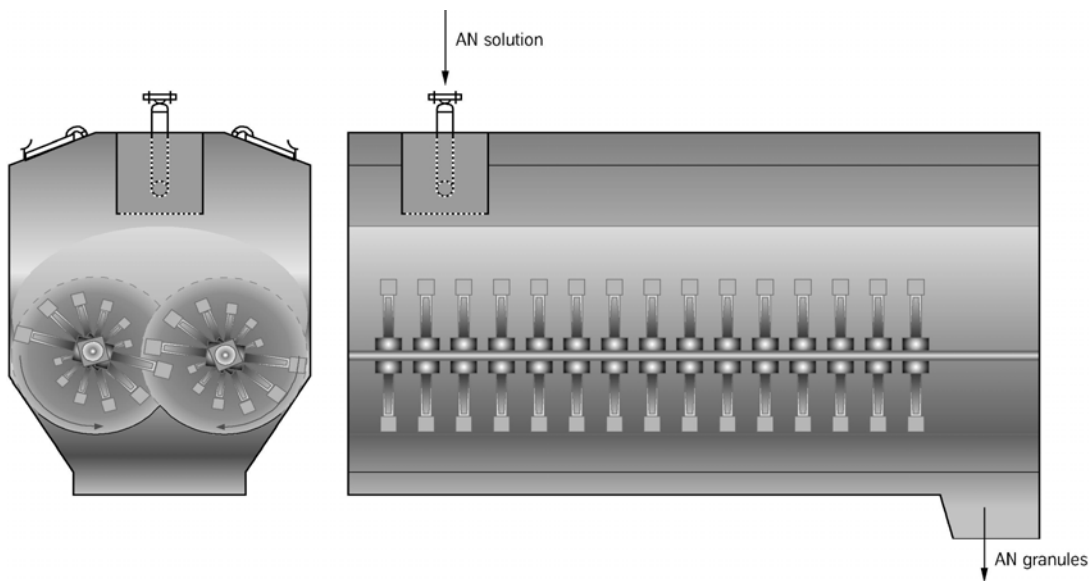
These differences in operating conditions of the two granulation routes have important consequences with regard to safety, production and maintenance.

- A high recycle process operates with lower ammonium nitrate concentrations, therefore the temperatures are significantly lower. Higher temperatures significantly increase the risk of ammonium nitrate decomposition.
- Lower temperatures also reduce the corrosive nature of the melt. This means that less expensive corrosion resistant materials can be used for critical equipment.
- In a high recycle processes, fines, oversize and off-spec material produced during granulation can be returned directly to the granulator. In a low recycle process these must be dissolved. This usually requires a large agitated tank. From this tank the solution is sent to the concentration section to reduce the water content. This always bears the risk that potentially contaminated material is introduced into hot AN solution.
- If the low recycle plant operates without a dryer, the amount of material which can be dissolved and returned to the process is limited by the water balance. Under upset conditions this can become a problem if too much over- or undersize material must be reprocessed. In this case the plant must be equipped with an off spec storage system to buffer this material until it can be reintroduced into the process. A high recycle process is usually designed with enough capacity to handle such upsets. As it contains a dryer the plant is not as water balance limited.
- In a high recycle process the filler can be introduced into the granulator without any heating. Due to the low AN concentration (= high water content) in the melt, this is even possible for grades with low N contents which require large amount of filler (up to 15-20% of production). In a low recycle processes producing low CAN grades with low N contents is difficult as the filler must be mixed with the AN solution before it enters the granulator. This requires a heated and agitated mixing vessel. However, just adding the filler would cool AN solution down to below crystallisation temperature. Therefore mixed AN/filler

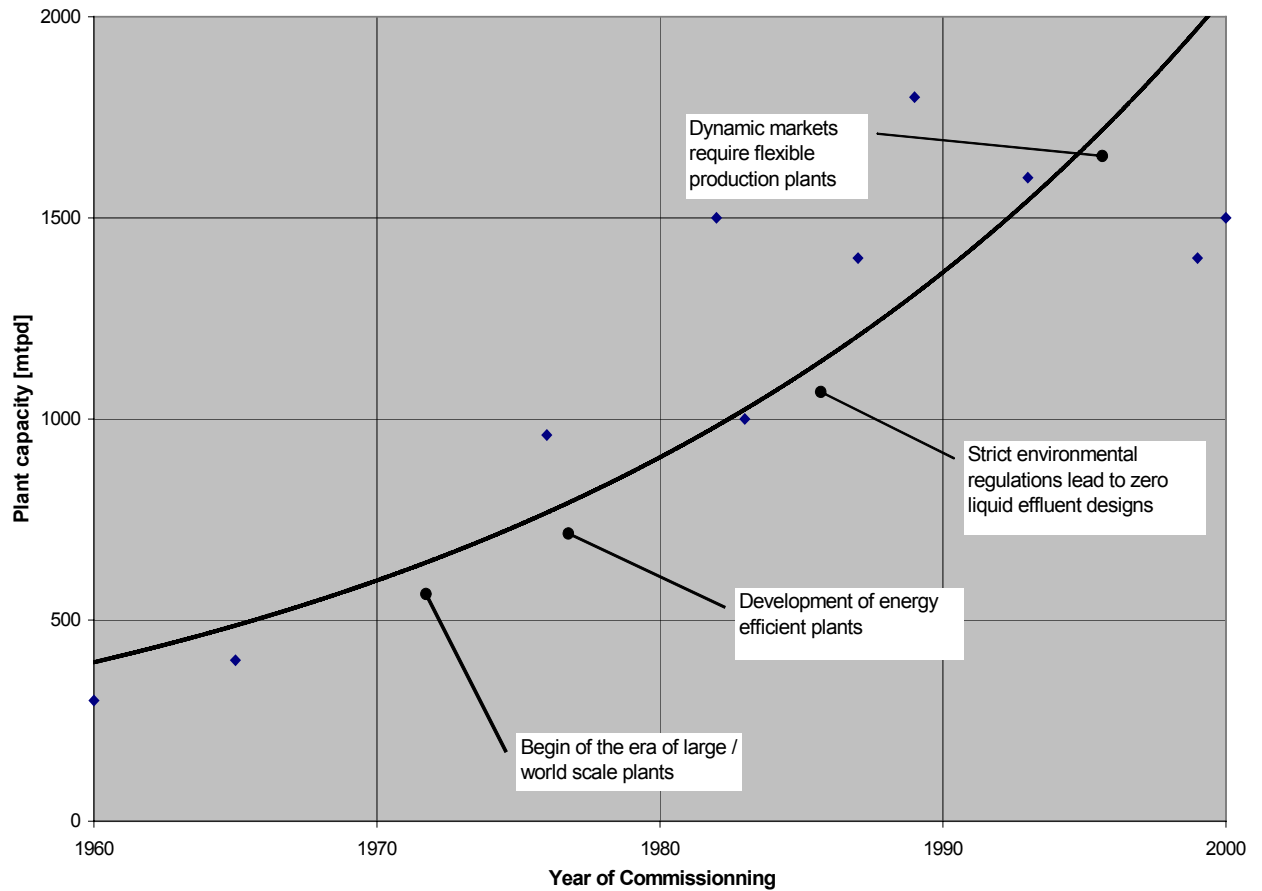
solution must be heated externally. This introduces an additional AN heat exchanger into the system.

- A high solid content in the melt leads to an increase in the amount of erosion occurring in the spray nozzles. This in turn causes the spray pattern to deteriorate. As this usually leads to bigger droplets and hence more coarse and lumpy particles are formed. Therefore the spray nozzles must be replaced regularly. The spray nozzles can also cause the formation of AN aerosol, which are extremely difficult to remove in a wet scrubbing system.
- Low recycle processes have the advantage of being able to add  $Mg(NO_3)_2$  to produce granular ammonium nitrate. This is a very effective method of stabilising ammonium nitrate as it changes the phase change temperature. This reduces caking and dust formation during storage and transport due to thermal cycling. However, it also increases the moisture pick-up of the product considerably, which is a particular problem for plants operating in or exporting to humid climate regions. This is also the reason why  $Mg(NO_3)_2$  cannot be used easily in a high recycle process. The higher residence time allows the  $Mg(NO_3)_2$  to diffuse to the grain surface. This leads to an excessive moisture pick-up in the dryer with the subsequent danger of blockages.

### 3. Development of State of Art Pugmill Granulation Process







In the course of this time period the industry has faced many major changes. Broadly these changes are shown in the following diagram. It shows the increase in capacity of a typical granulation plant for AN/CAN fertiliser. Also indicated are various developments due to financial or environmental influence that had a marked influence on the design of a modern AN/CAN granulation plant.

The inherent flexibility of the pugmill granulation plant design enabled it to meet all these challenges, which lead to the modern plant concept outlined in the next section.

#### 4. Details of a Modern Pugmill Granulation Process

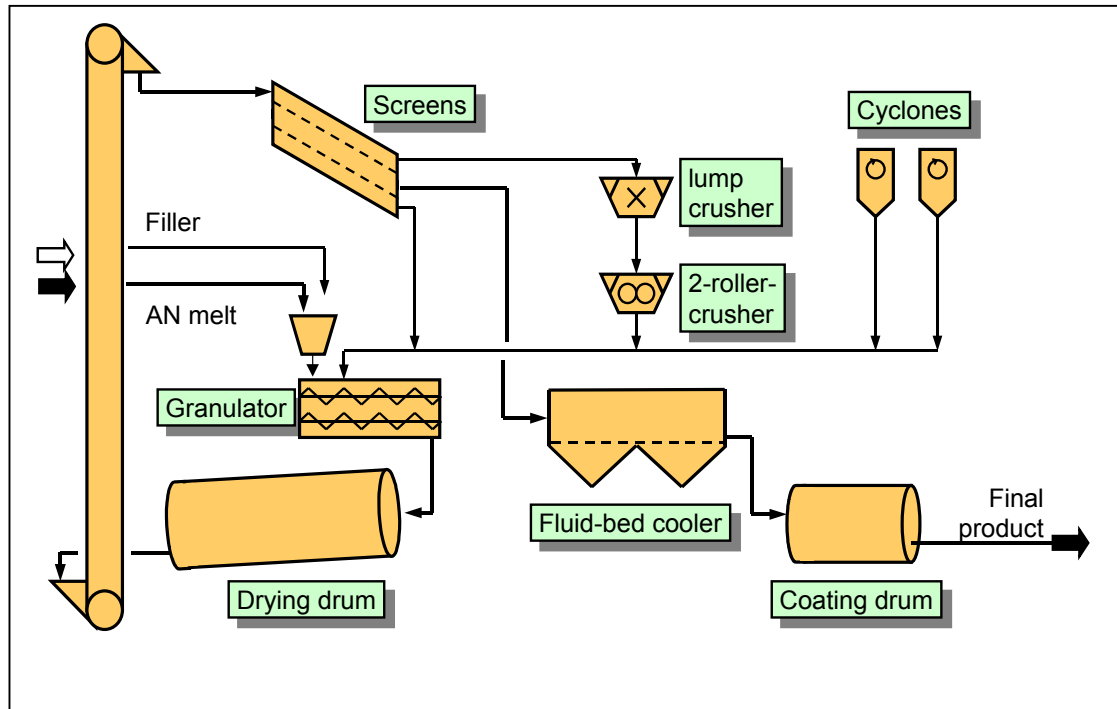


Figure 2: Granulation Flowsheet

A modern granulation plant consists of the following units:

- Granulation loop
- Product treatment
- Process air treatment
- Process water treatment
- Wash water treatment system

The granulation loop forms the actual product from AN melt, the required additives and the filler to adjust the N content. The main equipment of the loop contains the granulator and a dryer, screens crushers and the necessary transport equipment.

The product treatment section cools the product to the temperature required for storage. Subsequently, the product is usually treated with an anticaking agent and optionally with a coating agent.

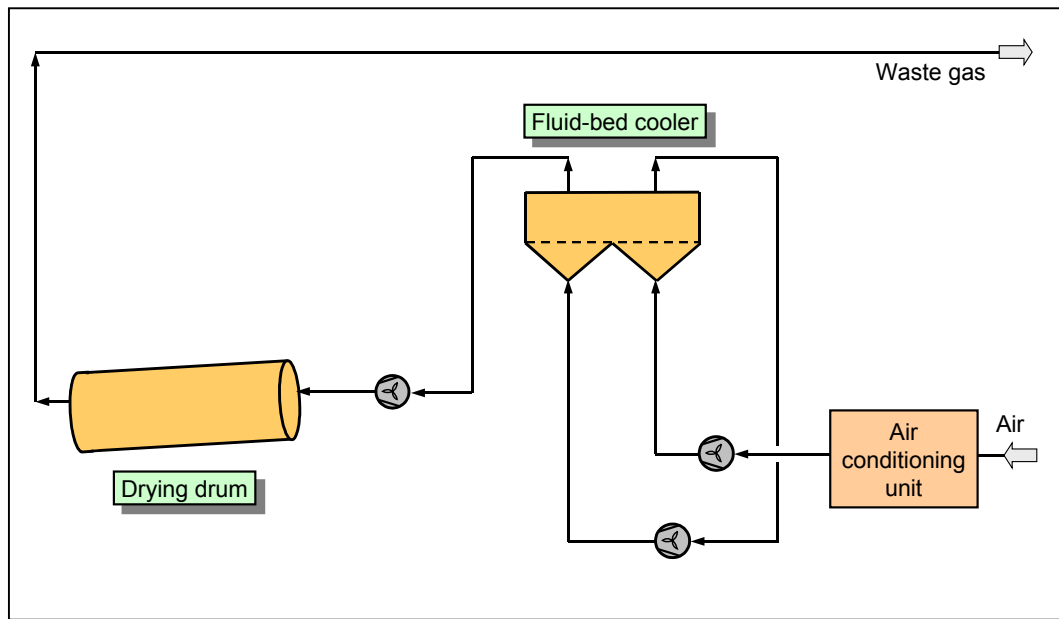


Figure 3: Air system

A significant feature of the Uhde process is that the offgas from the fluid bed cooler is used for drying the product in the dryer. This is a significant energy saving feature and enables the plant to run autothermally for nearly all CAN grades. This feature also effectively halves the amount of air that must be processed in the air treatment section.

Process air comes from the dryer and cooler and has to be treated to reduce the amount of  $\text{NH}_3$  and dust. A combination of cyclones and a wet scrubber are used to reduce the emissions. The cyclones remove most of the dust, whilst the scrubber takes care of the ammonia gases and the remaining dust.

The combination of cyclones and scrubber has the advantage that over 95% of the dust is recycled as dry matter and serves as seed material for the granulation. Only a small fraction of the dust is dissolved in the scrubber solution and is returned as a liquid suspension.

The filler dust consists of ammonium nitrate and filler. The calcium carbonate in the filler reacts with the acidic scrubbing solution to produce calcium according to the following reaction:



By reducing the amount of dust going to the scrubber the amount of calcium nitrate formed is therefore also reduced. The combination of cyclones and scrubber significantly reduces the formation of calcium nitrate in the scrubber. High calcium nitrate contents significantly increase the moisture uptake of the granules.

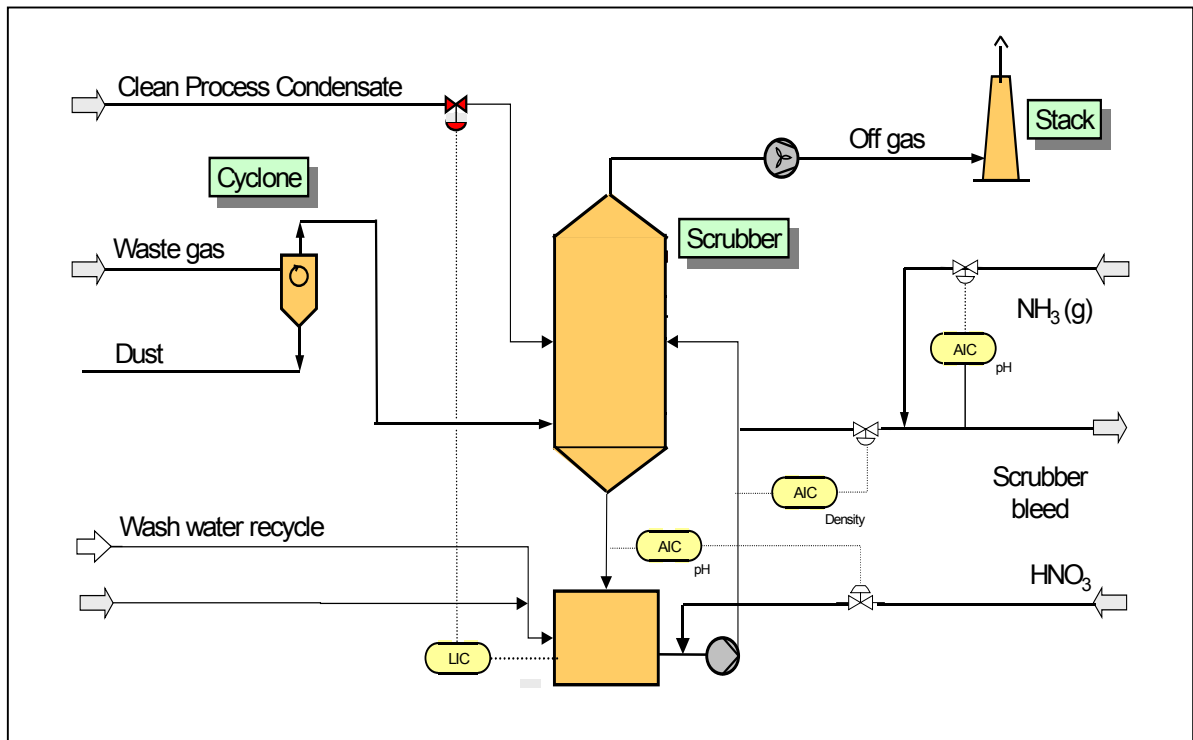


Figure 3: Air scrubbing system

All vapours from the concentration section are also treated in the wet scrubber. The scrubber consists of a packed bed section with an additional tray section to fine tune the system and eliminate aerosols.

To achieve zero liquid effluent operation all process water streams, e.g. the scrubber bleed, are collected and sent to a dedicated concentration section in the granulation plant.

All granulation plants must be cleaned from time to time. Due to the hygroscopic nature of AN the most efficient way is to use water. This discontinuous effluent stream can be discharged to a wastewater treatment plant, if such is available and has sufficient capacity. A better way is to collect the wash water in a pit or tank and reintroducing it into the granulation unit when the plant has resumed operation. From the pit the wash water is sent to the scrubber as make up water.

As the waste liquids contain large amounts of N in the form of AN, they can alternatively be used by local farmers to spray on their fields or processed in nearby NPK plants.

#### 4.1 Advantages of the Pugmill Process

All of the above features are incorporated into the design of a modern pugmill plant.

It is Uhde's opinion that the pugmill process is still the best option for producing CAN and related fertilisers.

- A pugmill plant is capable of producing the whole range of N contents from 22 - 33.5 %N.
- The pugmill process is very tolerant of the filler materials and additives. Most natural dolomites and limestone can be used. It can also process synthetic limestone from nitrophosphate plants.

- The addition of additives to achieve desired levels of sulphur or micronutrient is straightforward. These do not have to be added as solutions, but can be fed directly into the granulator.
- The process is inherently safer because it operates at low temperatures throughout (max. AN temperature is below 150°C).
- The high recycle makes the plant very stable and self-regulatory. All disturbances will even out over time and minor disturbances seldom require operator action.
- The kneading action of the pugmill produces a hard product.
- With few exceptions easily obtainable equipment can be used. The amount of proprietary equipment is very low.
- The pugmill plant is able to produce most CAN grades autothermally (i.e. no external heating required).
- The electrical power consumption is lower than for most other granulation processes.
- The reuse of cooler off-gas for drying reduces the air flows that must be treated in the scrubbing section considerably. This reduces the investment and operating costs.
- The emissions in the offgas from the scrubber are below Best Available Technology (BAT) levels.
- There are no liquid emissions during normal operation. All wash water solutions are collected and reprocessed.

## **5. Recent Research and Development**

### **5.1 Dolomite / Limestone Assessment**

An important part of the design of a new plant is the evaluation of the available raw materials, in particular the locally available filler material.

As described above many parameters play an important role for the selection of the filler and the subsequent design of the plant. Some of these are:

- The reactivity of the filler with AN and the amount of  $\text{Ca}(\text{NO}_3)_2$  formed during production.
- Its influence on the phase changes of AN, particularly the phase changes below 60°C i.e. the resistance against thermal cycling.
- The influence of  $\text{SiO}_2$  and other components on the product hardness.
- The effect on AN decomposition during production and storage.
- The effect on porosity and oil absorption.

To be better able to assess these parameters a laboratory programme has been set up to assess all filler material used in existing Uhde plants, but also potential material from previous and current projects. This knowledge has enabled us to generate a database, which currently contains the results of about 20 types of fillers from all over the world. As this programme is a continuous effort, the number of tested materials will increase continually.

With this knowledge we are in a position to assess available filler materials and to comment on their suitability during very early phases of the project. It also gives us an excellent reference base for the design of new plants.

## 5.2 New Granulation Additives

The pugmill process uses the additives  $\text{FeSO}_4$  and  $\text{AlSO}_4$  for the production of high N grade fertilisers, e.g. 33.5 % N. These are required as a granulation aid and for product stability. As explained previously  $\text{Mg}(\text{NO}_3)_2$  cannot be used in a high recycle process.

Although it is a very effective and cheap additive,  $\text{FeSO}_4$  gives the product a pinkish colour, which may not be acceptable in some markets. This, with the desire to simplify the process, has given us the impetus to seek other additives.

A promising development is the use of specific additives developed by the company NuFarm (previously called CFPI). Together with NuFarm, plant trials were conducted. In the trials the amount of  $\text{AlSO}_4$  and  $\text{FeSO}_4$  was reduced step by step with and without addition of their Galoryl additive.

Results show that, while it was not possible to completely replace  $\text{AlSO}_4$  and  $\text{FeSO}_4$  by Galoryl, the amounts added can be significantly reduced. This reduced the colour hue of the fertiliser and gave an almost white product.

We are certain, that with further modification of the Galoryl additive and an optimisation of process conditions the goal of eliminating one or both additives can be achieved.

## 5.3 Fertiliser with Sulphur

In recent years many soils have been showing a deficiency in sulphur. This has many causes, the most important being the switch from sulphur containing fertilisers like AS, SSP and TSP to straight N fertilisers: AN and urea. Another factor is the reduced sulphur emissions from electric power plants, as large-scale desulphurisation projects are showing an unexpected side effect.

This has spurred the recent demand for fertilisers containing sulphur. Despite the marketing efforts of some companies, elemental sulphur is not a good substance for plant nutrition. It takes at least 6 months before any effect is seen. Therefore various manufacturers have developed fertilisers with sulphur components. Some additives, which have been used, are kieserite or epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) or even bentonite. Another alternative is the use of gypsum.

A pugmill plant can produce S fertilisers, when one replaces part of the filler with a sulphur containing substance e.g. gypsum. To optimise this, plant trials were conducted. Using anhydrite gypsum the plant easily produced fertilisers with up to 6% S at full capacity. No changes to plant equipment or any significant changes to the process conditions were necessary. Currently development work is being undertaken to switch from anhydrite to the cheaper dihydrate gypsum.

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