Lecture 34

NPK Fertilizers – Mixed Acid route

INTRODUCTION

Straight fertilizers such as Calcium Ammonium Nitrate (CAN), Ammonium Nitrate (AN), Ammonium Sulphate (AS), Urea, Single Superphosphate (SSP), Triple Superphosphate (TSP), Potash (Potassium Chloride) (MOP) and combined types such as Mono-Ammonium Phosphate (MAP), Di-Ammonium Phosphate (DAP) are well-defined products made using well-defined processes. Compound or complex fertilisers such as NPK, are more difficult to define as there is an infinite number of N/P/K-ratios and the processes applied in their production are numerous.

The product name “NPK” is normally followed by three numbers to indicate the percent of N, P2O5 and K2O which the product contains, e.g. 24–6–12 indicates that this particular grade contains 24% N (nitrogen compounds), 6% P2O5 (phosphorus compounds) and 12% K2O (potassium compounds). In addition, the fertilizer may contain magnesium, boron, sulphur, micro-nutrients, etc. The typical content of nutrients (N + P2O5 + K2O) will normally be in the range of 40-60%.

Grades with no P2O5 or no K2O are also included in the “NPK” product range but they are normally named NP and NK fertilizers. These types of fertilizers can normally be produced in NPK plants and emission levels will typically be within the limits valid for NPK grades.

NPK fertilizers can be produced in four, basically different, ways:-

– Ammonium phosphate/ammonium nitrate-based NPK fertilizers
– Nitrophosphate-based NPK fertilizers (mixed acid route)
– Nitrophosphate-based NPK fertilizers (ODDA-route)
– Mechanical blending of single or multi-nutrient components

This chapter will only focus on the two first ways, which are characterised by the following technologies:-
1. Processing of raw materials
   – Mixed acid slurry processes with digestion of rock phosphate
   – Phosphoric acid slurry processes
   – Mixing of solid raw materials
2. Granulation techniques
   – Drum granulation
   – Blunger/pugmill granulation
   – Spherodiser granulation
   – Prilling

The selection of the basic techniques is based on several factors:
   – Target product range (N/P/K ratio)
   – Raw material basis
   – Quality parameters
   – Flexibility of process
   – Size of production plant
   – Integration with other processes
   – Economic factors

Nevertheless, having made a proper selection, almost all production sites will continue their own development to improve:
   – Production flexibility
   – Production efficiency
   – Environmental impact
   – Product quality

One NPK grade (15–15–15 / N–P2O5–K2O) using all the technologies is used in this Chapter to present comparable figures and the production rate has been standardised to 50t.h⁻¹.
Emission figures and production rates in a specific production unit will depend on the product grade, but the grade selected for this chapter can be considered an average grade. The raw material basis has also been standardized and only commercially available raw materials have been selected, although many production sites have access to other, alternative raw materials.

The technologies covered are all well-known and well-proven. The main developments within fertilizer technology have primarily taken place in the areas of instrumentation, process control (computers), measurement, waste recycling and gas cleaning. Many older plants have already been revamped and such developments have been incorporated.

The Chapter covers NPK production technology including gas scrubbing and materials handling equipment and the storage needed to handle solid raw materials and finished products. The Chapter does not cover the production of any intermediates such as nitric acid, phosphoric acid, sulphuric acid, ammonium nitrate solution or superphosphates.

This descriptions of technologies which can apply have been limited to three processes with the following characteristics.

1. Granulation with a pipe reactor system
   – Broad range of formulations
   – Direct neutralisation of phosphoric and sulphuric acid in a pipe reactor
   – No phosphate rock digestion
   – High costs of raw materials (P2O5)
   – Simple gas scrubbing
   – Low costs of labour and maintenance
   – Low cost of investment

2. Drum granulation with ammoniation
   – Broad range of formulations
   – Neutralisation of phosphoric and sulphuric acids in the granulation drum
   – No phosphate rock digestion
   – High costs of raw materials (P2O5)
– Simple gas scrubbing
– Low costs of labour and maintenance
– Low cost of investment

3. Mixed acid process with phosphate rock digestion
– Broad range of formulations
– Phosphate rock digestion enabling a considerable part of the phosphorus to be supplied from the low cost raw material, phosphate rock
– Flexible control of the reactions of raw materials in the liquid phase
– High product quality
– Complex gas scrubbing
– Medium costs of labour and maintenance
– Medium cost of investment

2. DESCRIPTION OF PRODUCTION PROCESSES BY MIXED ACID ROUTE

Three different processes are described:-
– Granulation with a pipe reactor system
– Drum granulation with ammoniation
– Mixed acid process with phosphate rock digestion

These three production principles can be combined with different types of granulation and drying equipment and different types of air effluent treatment systems. The descriptions are generalised but should cover a major part of the NPK fertilizer technologies (except the nitrophosphate process) which exist today.
2.1 Granulation with a Pipe Reactor System

This process works with a classical granulation loop but incorporates one or two pipe reactors. One pipe reactor is fitted in the granulator and another may be used in the dryer. (see Figure 1).

Phosphoric acid or a mixture of phosphoric and sulphuric acids is neutralised in the pipe reactors with gaseous or liquid ammonia. A wide range of grades, including ammonium phosphates, can be produced. The process is flexible and easy to operate and the pipe reactors can be operated with a high turn-down ratio.

2.1.1 Granulation and drying section

The required solid raw materials such as potassium chloride, potassium sulphate, superphosphate, secondary nutrients, micronutrients and filler are metered and fed into the granulator together with the recycle. The pipe reactor fitted in the granulator is designed to receive phosphoric acid, part of the ammonia, and all the other liquid feeds such as sulphuric acid and recycled scrubber liquor.

Concentrated ammonium nitrate solution may be added directly into the granulator and ammoniation rates in the pipe reactor vary according to the product. Further ammoniation may be carried out in the granulator.

A pipe reactor fitted in the dryer is fed with phosphoric acid and ammonia. The N/P mol ratio is 1.00 (essentially producing mono-ammonium phosphate). The MAP produced consists of very fine particles and passes via the cyclones and screens back to the granulation drum. The granules obtained are dried in a drying section using a heated air stream.

2.1.2 Screening, crushing, cooling and coating

The dry granules are screened into three fractions. The over-size is removed and returned via the crusher to the granulator, together with the fines. The product-sized fraction is removed with the possibility of returning part of this fraction to the granulator to stabilize the recycle loop. Finally the on-spec fraction is cooled in classical cooling equipment such as a fluidized bed cooler or a cooling drum. The cooled product is fed into a coating drum where a surface coating is applied to prevent caking.
2.1.3 Gas scrubbing and dust removal
Gases from the granulator and the dryer are scrubbed in venturi scrubbers with recirculating ammonium phosphate or ammonium sulfo-phosphate solution. Make-up phosphoric and/or sulphuric acid is/are added for pH control if necessary. The scrubber liquor which is being recycled is fed to the pipe reactor in the granulator. Finally, the gases are vented through cyclonic columns irrigated with an acidic solution.

The gases coming from the dryer are de-dusted in high efficiency cyclones to remove the majority of the dust before scrubbing. The air coming from the cooling equipment is generally recycled as secondary air to the dryer after de-dusting. General de-dusting equipment is installed in the entire plant.

2.2 Drum Granulation with Ammoniation
This process consists of a classical granulation loop using mainly solid raw materials. Ammonium nitrate solution and/or steam is/are fed into the granulator. The process is very flexible, and is able to produce a broad spectrum of grades including products with a low nitrogen content. (see Figure 2).

2.2.1 Granulation and drying
The required solid raw materials such as potassium chloride, potassium sulphate, superphosphates, ammonium phosphates, secondary nutrients, micronutrients and filler are metered and fed into the granulator together with the recycle. Ammonium nitrate solution is sprayed directly into the granulator and sulphuric acid may be fed into the granulator followed by ammoniation. For some NPK grades steam is also used to keep the temperature at the required level. The granules obtained are dried in a drying section using a heated air stream.

2.2.2 Screening, crushing, cooling and coating
The dry granules are screened into three fractions and the over-size is removed and returned via the crusher to the granulator together with the fines. The product-sized fraction is removed with the possibility of returning part of this fraction to the granulator to stabilise the recycle loop. Finally, the on-spec fraction is cooled in classical cooling equipment such
as a fluidised bed cooler or a cooling drum and the cooled product is fed into a coating drum where a surface coating is applied to prevent caking.

2.2.3 Gas scrubbing and dust removal

Gases from the granulator and dryers are scrubbed in venturi scrubbers with recirculating ammonium phosphate or ammonium sulpho-phosphate solution. Makeup phosphoric and/or sulphuric acid is/are added for pH control if necessary. The scrubber liquor which is being recycled is fed into the granulation drum. The gases coming from the dryer are de-dusted in high efficiency cyclones to remove the majority of the dust before scrubbing. The air coming from the cooling equipment is generally recycled as secondary air to the dryer after de-dusting. General de-dusting equipment is installed in the entire plant.

2.3 Mixed Acid Process with Phosphate Rock Digestion

This process is very flexible and produces grades with varying degrees of phosphate water solubility. The process is able to use cheap raw materials such as phosphate rock (see Figure 3).

2.3.1 Phosphate rock digestion and ammoniation

This type of process is characterised by the way the phosphates, or at least a part of them, are made “available” (soluble). The first step of the process is the digestion of phosphate rock with nitric acid resulting in a solution of phosphoric acid and calcium nitrate. Acid gases such as oxides of nitrogen and fluorine compounds are formed during the digestion, depending on the type of phosphate rock.

Other raw materials such as phosphoric, sulphuric and nitric acids or AN solution are added after the digestion, which is an exothermic process. The acid slurry is ammoniated with gaseous ammonia and after neutralisation, other components such as ammonium phosphates, superphosphates, ammonium sulphate and compounds containing potassium and magnesium, are added. Most of these materials may also be added before or during neutralisation but if the raw material contains chloride the pH of the slurry should be 5 – 6 to avoid the production of hydrogen chloride. The design of the reactor battery can vary from a few large reactors to many, smaller reactors. Common for all the designs of the reactor battery is that the row of reactors ends with a buffer tank.
Depending on the type of raw material, the amount of gas scrubber liquid to be recycled and the degree of ammoniation, the water content of the slurry in the buffer tank can vary between 5% and 30% and the temperature from 100°C to 140°C.

2.3.2 Granulation, drying, screening, crushing, cooling and coating

In principle, the dry section can be divided into a granulation part, a drying part, a screening/crushing part, a cooling part and a coating part. The granulation can be performed by different equipment such as drum, blunger and Spherodiser. The Spherodiser granulation also incorporates the drying operation. A broad spectrum of grades can be produced by these processes, but NPK fertilizers with a very low content of nitrogen are not convenient for the spherodiser process because in such cases a sprayable slurry will demand an unrealistic, high content of water.

In all the granulation processes mentioned above the off-spec fraction from the screening/crushing operation is recycled to the granulation equipment. All granulation processes, except the spherodiser process, require a drying operation after the granulation. This drying is normally carried out in a drying drum. The fertilizer may be cooled in a cooling drum or in a fluidised bed cooler. The coating can be a combination consisting of a treatment with an organic agent and an inorganic powder. Both additions can be made in one drum.

2.3.3 Gas scrubbing and dust removal

2.3.3.1 Reactor gases

The gases from the digestion reactors, where phosphate rock is digested in nitric acid, are treated separately in a spray tower scrubber to recover NOx and fluorine compounds. The pH is adjusted by the addition of ammonia.

The ammoniation reactor gases are scrubbed in several stages of counter-current scrubbing. The pH is adjusted to the most efficient scrubbing condition, pH 3-4, with a mixture of HNO₃ and/or H₂SO₄. The first scrubbing stage ensures a saturation of the gases; the second high pressure venturi stage is designed to remove aerosols. The subsequent stages make the recovery efficiency high and the final stage operates with the cleanest scrubbing liquid. A droplet separator is installed in the stack or immediately before it.
2.3.3.2 Drying gases
The gases from the dryer (granulator/dryer) are led through cyclones before entering the scrubber. The scrubber consists of a variable throat venturi with subsequent two-stage scrubbing. The last stage should be operated with the cleanest liquid. A part of the liquor, after the circulation, goes to a settler for the separation of solids. The thickened part is fed to the reactors and the overflow returned. The pH is adjusted with acids to pH 3-4.

2.3.3.3 Cooling gases
The cooler uses ambient air or cooled and conditioned air. The warm air from the cooler is recycled to the inlet of the dryer.

2.3.3.4 General de-dusting
Screens, crushers and conveyor discharge points are de-dusted and the de-dusting air is cleaned in a bag filter before recycling or discharge into the atmosphere.