Lecture 35

NPK Fertilizers – Nitrophosphate Route

Phosphate sources must be converted into a form which can be taken up by plants (“available”). This can be achieved by using the integrated “Nitrophosphate” process which produces compound fertilizers containing ammonium nitrate, phosphate and potassium salts. This process aims to produce nitrate-containing straight and compound fertilizers starting from rock phosphate and using all the nutrient components in an integrated process without solid wastes and with minimal gaseous and liquid emissions.

The integrated process starts with the dissolution of the rock phosphate in nitric acid following the reaction:-

\[ \text{Ca}_5\text{F(PO}_4\text{)}_3 + 10\text{HNO}_3 \rightarrow 3\text{H}_3\text{PO}_4 + 5\text{Ca(NO}_3\text{)}_2 + \text{HF} \]

Varying amounts of volatile compounds such as carbon dioxide (CO2), nitrous gases (NOX) and hydrogen fluoride (HF) may be liberated, depending on the rock phosphate. The mother liquor obtained contains too many calcium ions to guarantee the production of plant available P2O5. The solution is therefore cooled so that calcium nitrate tetrahydrate (CNTH) crystallises out following the reaction:-

\[ \text{H}_3\text{PO}_4 + \text{HNO}_3 + \text{Ca(NO}_3\text{)}_2 + 4\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + \text{HNO}_3 + \text{Ca(NO}_3\text{)}_2.4\text{H}_2\text{O} \]

The solution of phosphoric acid, remaining calcium nitrate and nitric acid, called nitrophosphoric acid, can be separated from the CNTH crystals by filtration. The nitrophosphoric acid is then neutralised with ammonia, mixed with potassium/magnesium salts, sulphate and/or micro-nutrients and converted in a rotary granulation drum, fluidised bed, prilling tower or pug-mill to obtain solid compound fertilizers containing nitrate.

The separated calcium nitrate crystals are dissolved in ammonium nitrate solution and treated with ammonium carbonate solution following the reaction:-

\[ \text{Ca(NO}_3\text{)}_2 + (\text{NH}_4\text{)}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NH}_4\text{NO}_3 \]
This solution is filtered and the calcium carbonate crystals are removed and used for the production of granular calcium ammonium nitrate fertilizer. The resulting dilute ammonium nitrate solution is concentrated and also used to produce calcium ammonium nitrate fertilizer or NPK.

The calcium nitrate solution may also be neutralised and evaporated to obtain a solid fertilizer. Depending on the phosphate rock and the cooling temperature around 2.2 tonnes of calcium carbonate or 3.6 tonnes of calcium nitrate per tonne of P2O5 are obtained.

**Production Processes**

**Nitrophosphoric Acid Production Unit:**

This unit contains two important production stages:-

– The production of calcium carbonate

– The production of concentrated ammonium nitrate solution

**2.2.4.1 Production of calcium carbonate**

As described above, calcium nitrate tetrahydrate crystals are separated from the nitrophosphoric acid solution by various separation techniques. These crystals are dissolved in an ammonium nitrate solution and pumped to a storage tank. In another section of the plant a solution of ammonium carbonate in dilute ammonium nitrate is prepared. Carbon dioxide from an ammonia plant and gaseous ammonia from the refrigeration section of the nitrophosphoric unit are the raw materials for the ammonium carbonate production. Around 1.0t of CO₂ is used per tonne P₂O₅ produced.

The ammonium carbonate solution is mixed with the calcium nitrate solution and the following reaction takes place:-

\[
\text{Ca(NO}_3\text{)}_2 + (\text{NH}_4\text{)}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NH}_4\text{NO}_3
\]
The resulting reaction mixture passes to a belt filter where the precipitated CaCO3 is filtered off. The calcium carbonate is sent to storage before being used in the production of granular calcium ammonium nitrate or in other applications. The remaining ammonium nitrate solution (50-65% AN) is pumped to a storage tank and can be used for the production of compound fertilizers or calcium ammonium nitrate. This production stage has no liquid effluents because all the water used is recycled in the different production stages. Nevertheless, the carbonisation and conversion sections have off gases which are treated in a scrubbing column and the scrubbing liquor is recycled. The off gases, containing small amounts of NH3 and F after scrubbing, are discharged to atmosphere.

2.2.4.2 Production of concentrated ammonium nitrate solution

The solution from the belt filter is treated in a second filtration step to remove the remaining CaCO3 crystals. The excess ammonium carbonate is neutralised with nitric acid and the resulting neutral clean dilute ammonium nitrate solution is stored in an AN solution tank from where it is pumped to the AN evaporation section. The AN evaporation section may consist of a series of falling film evaporators and may constitute a double or triple-effect evaporation depending on the capacity and cost of energy at the given location. Saturated steam of max. 9bar, provides the necessary energy for this concentration unit. The concentrated AN solution can be stored before use in the production of granular fertilizers. This section has practically no emission into air. Liquid effluents are generated by the condensation of the evaporated gases and are normally recycled, used for cleaning purposes, purified by an appropriate method and/or sent to a biological treatment plant.
Lecture 26

NPK Fertilizers – Nitrophosphate Route (Part 2)

The production process of N

2.2.5 Compound fertilizer production unit

Nitrate containing fertilizers can be produced from the nitrophosphoric acid produced as described in Section 2.2.3, by neutralising with ammonia and with the possible addition of nitric acid, ammonium sulphate or sulphuric acid, potassium and magnesium salts and micronutrients. This production is carried out in three sections; neutralisation, particle formation and conditioning.

2.2.5.1 Neutralisation

The nitrophosphoric acid solution with a CaO/P2O5 ratio of 0.21-0.65 is neutralised with gaseous ammonia to around pH 5 in stainless steel reactors in different stages. This reaction is very exothermic and raises the temperature to around the boiling point (125-145°C). The reaction heat is normally used for economic evaporation of the slurry and cooling the slurry. More or less water is evaporated depending on the kind of granulation, so that after mixing the solution with potassium salts and other nutrients the following water contents are reached:-

– Spherodiser : 10-28%
– Granulation drum : 4-12%
– Prill tower : 0.5%

All the processes involve treatment with ammonia and operate at high temperature, generating off-gases. It is possible to use various condensing or scrubbing systems for these offgases as the different kinds of processes work under different conditions. Energy costs, type of raw material, investment costs, type of granulation and the grades of fertilizers all
influence the choice of the emission reduction technique. The recycling of the condensates or scrubber liquor is dependent on the water balance of the grade which is produced.

2.2.5.2 Particle formation

Three types of processes are normally used for the production of NPK fertilizers; prilling, drum or pugmill granulation and Spherodiser granulation. The three types of particulation give different amounts of emissions to air and require different treatment systems. The air and water emission levels proposed in Chapter 8 are levels for all the particulation processes.

*Prilling*

Evaporated NP liquor from the neutraliser is mixed with the required salts and recycled product. The final water content is about 0.5%. The mixer overflows into a rotating prill bucket from which the slurry is sprayed into the prill tower. Fans at the top of the tower cause ambient air to flow counter-current to the droplets formed by solidification. The solid prills fall onto a rotating tower bottom and are scraped off and forwarded to the dry handling system. The product leaving the prilling tower is screened to meet product specifications. Over- and under-size material is returned to the process and the on-size NPK product is sent to the conditioning section.

Dust emission from the prilling tower itself is very low. No special air treatment system is needed for the vast amounts of cooling air because the dust concentration is less than 5mg.Nm⁻³. Total dust emission is dependent on the ammonium nitrate content and is normally less than 2.5kg.h⁻¹ as the total air volume passing through the prilling tower is more than 500,000Nm³.h⁻¹. The concentration of ammonia is also low, being typically 10-15mg NH₃.Nm⁻³ (5-7.5kg.h⁻¹). The amount of ammonia escaping is related to several process parameters, especially pH, high temperature and the NH₃/P₂O₅ ratio of the NP liquors. Recovery of ammonia from such large volumes is unrealistic and the only way to minimise this ammonia loss is to control the pH.
**Drum and pugmill granulation**

The NP liquor at approximately 135°C and with a water content around 4-12% is mixed with the required salts and recycled products and is pumped and sprayed into a rotating drum granulator. The water evaporated in the drum is carried away by a co-current flow of air. The granules so formed are dried in a rotating drying drum with hot air. The water content of the granules is normally below 1.5%. The air leaving the drums, about 100,000 Nm³.h⁻¹ for the production of 55t.h⁻¹ 15-15-15, contains water vapour, dust, ammonia and combustion gases. The air from the granulation and drying drums is treated in high performance cyclones, giving low dust levels (< 50mg.Nm⁻³) after passing the cyclones. As with the prilling tower, the amount of ammonia lost in the granulation and drying drum depends on the operating temperature and the final pH of the neutralised slurry. The average ammonia content is less than 150mg.Nm⁻³ under normal conditions, if the final pH is maintained at about 5.0. The NPK product, after drying, is screened and the onsize hot product is sent to the conditioning section. The under-sized and over-sized granules, are returned to the granulator after crushing. Screens, crushers and conveyor discharge points are de-dusted in one mode of operation using the air going to the drums.

**Spherodiser granulation**

The NP liquor with a temperature of 115-120°C is mixed with the required salts and recycled products. The resulting slurry with a water content of 10-28% is pumped and sprayed into a special rotating drum, called a spherodiser. Warm air, heated to 300-400°C by gas or fuel flows co-currently in the spherodiser evaporating the water from the NP liquor and building up dry granules with a water content of <1.5%. The air from a spherodiser, about 100,000 Nm³.h⁻¹ is treated in high performance cyclones. The
remaining dust and NH3-content is dependent on the grade, the operating temperature and pH of the NP liquor. The dry granules are screened and the over-size taken out, crushed and returned to the spherodiser together with the under-size. The on-size fraction passes to the conditioning process. The screen, crusher and conveyor discharges are de-dusted using the air required for granulation.

2.2.5.3 Conditioning

The commercial product from the drying and screening is cooled in a fluidised bed, a bulk flow heat exchanger or rotating drum. Off-gases from these latter stages, containing minor amounts of dust and generally no ammonia, are de-dusted in cyclones. Finally, the product is cooled and coated before storage in order to minimise the subsequent caking of the material.

2.2.6 Calcium nitrate fertilizer production unit

The calcium nitrate crystals from the nitrophosphate process can be processed to a solid calcium nitrate (CN) fertilizer, using prilling or pan-granulation technology, as an alternative to the combination of CNTH conversion and subsequent processing to CAN

2.2.6.1 Neutralisation and evaporation

The CNTH crystals from the nitrophosphoric acid unit are heated to form a melt which is pumped to a two-stage atmospheric tank reactor system for neutralisation with gaseous ammonia. The reaction between ammonia and the remaining acids in the CNTH melt is exothermic. The ventilation gases from the two reactors are scrubbed with water before being discharged to atmosphere. The total discharge from the scrubbers is <0.3kg.h-1 (NO3-N and NH4-N) for a 100t.h-1 plant and the concentration is <35mg N.Nm-3 of off-gas. The 60% CNTH melt, containing small amounts of ammonium nitrate is evaporated in one or two stages to a final concentration of 85% and this concentrated solution is then transferred to the prilling or pan granulation process.
The process steam containing ammonia is scrubbed with condensate and compressed for energy recovery for use in the evaporators. Part of the condensate is discharged into water and the remainder is returned to the process. The discharge of NO3 and NH4 nitrogen into water from a 100t.h-1 CN plant is around 30kg.h-1, when a spillage collection system is installed in the wet part of the process. The collected spillage is returned to the process.

2.2.6.2 Pan granulation

The concentrated melt from the evaporator system is sprayed into the pan granulator together with the recycled fines. The granules are smoothed in a smoothing drum and air-cooled in a fluid bed. The cooled product is screened in two stages and the on-size product is transferred to a coating drum and finally to storage. The over-size material is crushed, mixed with the fines and recycled to the granulator.

The ventilation gases from the granulation and dry part of the process are scrubbed with water and process condensate from the wet part of the process, in a lamella separator before discharge to atmosphere. The emission of CN-containing aerosols to air is normally <4mg NO3-N.Nm-3 of off-gas. The volume of ventilation air from a pan granulator producing 50t.h-1 CN fertilizer is 170,000Nm3.h-1. The condensate from the lamella separator, containing calcium nitrate, is mixed with collected spillage from the dry part of the process and returned to the neutralisation section. There is no discharge of NO3-N into water from the dry part of the process.

2.2.6.3 Prilling

The concentrated melt from the evaporators is mixed with recycled fines and fed to a rotating prill bucket. The melt leaving the bucket solidifies due to the heat exchange with counter-current air in the prill tower. Air from the prill tower is discharged to atmosphere without dust removal. The volume of air from a 40t.h-1 CN plant is 370,000Nm3.h-1, normally with a CN dust concentration of 20mg.Nm-3. The prills from the base of the
tower are cooled with air in a fluid bed cooler and screened to remove off-size material. The product-size prills are coated before storage. Over-size material is dissolved in neutralised CN solution and returned to the evaporator feed tank. Undersize material is mixed into the evaporated melt before prilling.