Lecture 23

Nitrophosphate Fertilizers – Part 1

Introduction

“Nitrophosphate” is the generally accepted term for any fertilizer that is produced by a process involving treatment of phosphate rock with nitric acid.

Fundamentals of Nitrophosphates

The basic (and simplified) acidulation reaction can be represented by the following reaction equations:

\[
\text{Ca}_3(\text{PO}_4)_2 + 4 \text{HNO}_3 \rightarrow 2 \text{Ca(NO}_3)_2 + \text{Ca(H}_2\text{PO}_4)_2 + 20.2 \text{kcal}
\]

\[
\text{Ca(H}_2\text{PO}_4)_2 + 2 \text{HNO}_3 \rightarrow \text{Ca(NO}_3)_2 + 2 \text{H}_3\text{PO}_4 + 2.05 \text{kcal}
\]

Overall

\[
\text{Ca}_3(\text{PO}_4)_2 + 6 \text{HNO}_3 \rightarrow 3 \text{Ca(NO}_3)_2 + 2 \text{H}_3\text{PO}_4 + 22.25 \text{kcal}
\]

After separation of the insoluble material, phosphoric acid is neutralized with ammonia to produce a fertilizer. If the calcium nitrate is left in the solution, it reverts to dicalcium phosphate ammonium following the reaction:

\[
2\text{H}_3\text{PO}_4 + \text{Ca(NO}_3)_2 + 4\text{NH}_3 \rightarrow \text{CaHPO}_4 + (\text{NH}_4)_2\text{HPO}_4 + 2\text{NH}_4\text{NO}_3 + 66.67 \text{kcal}
\]

Calcium is non-nutrient in terms of N, P, and K and is therefore seen as a diluent. For these reasons alone, it is desirable to remove calcium from the solution. But there is another, more important reason. If the calcium nitrate is left in the solution, when it is neutralized the N:P ratio will be fixed. To produce grades with lower N:P ratios, it is necessary to remove calcium nitrate, whereas if higher nitrogen grades are required, the removed calcium nitrate can be converted to ammonium nitrate and returned to the
solution. Therefore, most nitrophosphate processes include some means of removing calcium nitrate from the solution.

**Nitrophosphate Processes**

**Selection of Phosphate Rock**

In general, reactivity of the phosphate rock is no problem; even igneous apatites dissolve readily in nitric acid. The rock need not be finely ground; rock finer than 1 mm is satisfactory, and some operators even accept particles up to 4 mm. In general, the rock need only be fine enough to prevent rapid settling in stirred reaction vessels. High-silica rock can be used if the equipment is designed for that purpose. Most nitrophosphate plants include a silica removal step. Coarse silica particles can be very abrasive to pumps and piping, and this fact should be considered in plant design.

It is desirable that the CaO:P₂O₅ ratio in the rock should be as low as economically feasible to minimize the amount of calcium that must be removed or offset (in mixed-acid processes). While additional calcium requires more nitric acid, it does not necessarily involve a direct economic penalty because the nitrate is subsequently converted to ammonium nitrate either in the nitrophosphate product or in a coproduct.

Carbonates in phosphate rock cause foaming, which is usually dealt with by using mechanical foam breakers. However, foaming can be a difficult problem with some rocks.

Organic matter is undesirable in nitric phosphate processes; it reacts with nitric acid with emission of nitrogen as NO₂ or other nitrogen oxides.

Iron and aluminum oxides present no special problem within the range of occurrence in commercial phosphate rocks; these oxides usually are dissolved in nitric acid and reprecipitated during ammoniation as citrate-soluble phosphates. TVA tested “leached-zone” Florida phosphate containing a high percentage of aluminum phosphate minerals in a special nitrophosphate process.
Process Alternatives

The two commercially important nitrophosphate processes differ in the way they solve the problem of phosphate water solubility caused by the presence of calcium nitrate in the slurry resulting from the reaction of phosphate rock with nitric acid. The first process, historically, is the Odda process wherein calcium nitrate is precipitated and separated. The “mixed acid“ process does not separate the calcium nitrate; the phosphate water solubility is increased by adding phosphoric acid to decrease the Ca:P$_2$O$_5$ ratio.

Odda Process With Calcium Precipitation

Dissolving Section

In the dissolving section phosphate rock and nitric acid are mixed together in the dissolving reactors. Nitric acid of about 60% concentration is used in slight stoichiometric excess. The temperature in the reactors is kept constant at 60°-70°C by cooling or heating NITRIC ACID. In addition to fresh nitric acid, wash acid from the inerts filter and from the calcium nitrate tetrahydrate (CNTH) filter is fed to the reactors.

The dissolving solution contains suspended solids, mostly quartz, originating from the rock. Quantity and size of the solids vary with the source of rock. Inerts act as an undesirable diluents of nutrients in the final product and can cause damage to equipment and piping by erosion.

Inerts are separated from the dissolving solution by gravity in lamella separators; the clear solution overflows into the dissolving solution storage tank, and a thickened inerts slurry is washed out to a belt filter or to hydroclones. Sand is washed with nitric acid and a small amount of water, and, if necessary, washed to neutral in a batch washing tank. The liquid effluent from the washing tank is sent to the effluent treatment plant. Inerts are sold, eg., to the building industry.
The submerged part of the reactor may be made of low-grade stainless steel. The top part of the reactor, which is in contact with reaction gases that contain NO$_x$ and fluorine compounds, must be made of appropriate more resistant material.

**Crystallization Section**

Dissolving solution (NP solution) is fed intermittently to a number of batch-operated standard crystallizers. Cooling for crystallization is obtained by evaporating ammonia for the NP solution neutralization and calcium nitrate (CN)-conversion sections. The balance is supplied by a refrigeration system, if required.

The crystallization process is entirely computer controlled. The coldest crystallizer, having obtained the required final temperature, discharges to the filter head tank. The final temperature is fixed, e.g., -2° to -5°C when about 80% water-solubility is required, or +2°C when about 70% water-solubility is sufficient. Separation of crystals is done on a belt filter using several washing zones or with drum filters in series. Cold nitric acid and CN-solution are used as washing liquid. NP acid, the product from the filter, is stored in the NP acid storage tank. To fine tune the NP-acid quality (CaO/P$_2$O$_5$-ratio), dissolving solution is passed over the crystals. The separated CNTH crystals are dissolved in the dilute ammonium nitrate solution to form the CN solution.

**Neutralization Section**

In the neutralization section, the nitrogen and phosphorous elements in the NP solution are converted to the form they will have in the product. Correct operation of this section is important because the N:P$_2$O$_5$ ratio of the final product is controlled here. This control is achieved by mixing NP acid obtained from the CNTH-filters with ammonium nitrate solution and with an original dissolving solution. Neutralization by gaseous ammonia occurs in a pressurized reactor at 1.5-2.5 bar and a temperature of 150°-180°C or in forced-circulation neutralizers. Because of the heat of reaction, water and ammonia are evolved during neutralization; this decreases the water content of the slurry which is then further concentrated in a series of circulating evaporators.
The neutralization and evaporation operations have their own scrubber system for off-gases. The scrubbing liquor is composed mainly of ammonium nitrate solution, which is later recycled to the neutralization section for nutrient recovery.

**Finishing Section**

The final slurry after ammoniation and evaporation is formed into granules, with or without addition of potash salts, by a variety of methods including:

- Granulation in a pugmill or blunger.
- Ammoniation and granulation in a rotary drum.
- Granulation and drying in a Spherodizer®.
- Granulation and drying in a spouted bed system.

**Prilling of a melt. Calcium Nitrate Conversion and Calcium Ammonium Nitrate (CAN) Unit**

The CN-conversion and CAN units contain the following sections:

- **CN Conversion Unit**
  - Ammonium carbonate preparation section
  - CN-conversion section
  - Lime separation section

- **CAN Unit**
  - AN concentration section
  - Additives preparation section
  - Mixing, granulation (or prilling), and drying section
  - Cooling, screening, and coating section
Off-gas treatment section

CN-conversion section begins with the preparation of ammonium carbonate solution in a dilute ammonium nitrate solution in a packed carbonation tower with external circulation. Heat exchangers are used to control the temperature gradient over the tower. Raw materials are carbon dioxide and gaseous ammonia evaporated in the refrigeration section. The required ammonium carbonate solution is taken from the circulation loop and sent to the conversion reactor with the corresponding quantity of CN solution. A lime settler and a vacuum filter separate the reaction products, dilute ammonium nitrate solution, and calcium carbonate (lime). The AN-solution obtained here requires a second filtration step on precoat is established with the product lime itself. After this second filtration step the remaining ammonium nitrate is stored in the AN-solution tank; from there it is pumped to the AN evaporation section and to the CNTH-filter to dissolve fresh calcium nitrate tetrahydrate crystals.

The CN-conversion section has its own packed off-gas scrubber with external circulation. The scrubber liquid is an acidified dilute AN-solution, which is returned to the process.

The AN-evaporation section consists of several falling film evaporators in series. The first part of this section produces a concentrated AN-solution of 93-94 wt% AN. Depending on the capacity and cost of energy, this step may consist of double- or triple-effect evaporation. Each falling film evaporator set consists of a preheater, heater/ evaporator, vapor separator and transfer pump. A two-stage water ring vacuum pump provides the necessary vacuum, and a steam saturator, operating at 0.9 MPa absolute (175°C condensing temperature), provides the necessary energy for the concentration unit.

The ammonium nitrate solution at 93-94 wt % is stored and pumped to the second part of the evaporation unit and/or to the NP-unit. This second part is
composed of one falling film evaporator with the separator operating at 0.3 bar (absolute) and concentrating up to the required concentration of about 98 wt %. Steam is removed from a separate steam saturator at 9 bar (absolute). The vacuum system of this section can be combined with that of the first part.

CAN-slurry is produced in a mixing section, which consists of dissolving vessels for additives and feeding equipment for gypsum, which is added to the lime. Dissolved additives, lime/gypsum mixture and concentrated AN-melt are delivered to a mixing vessel with an agitator. From there it flows into a second vessel and is then circulated back to the mixing vessel. CAN slurry for granulation is taken from this circulation loop.

The CAN granulation section uses a granulation drum with internals to produce a screen of falling materials, on which the concentrated CAN slurry is sprayed. The granules that are produced fall by gravity into a counter currently operated drying drum. The drying drum is operated autothermally, which means that no external heat source is required to preheat the drying air. Off-gas from the dryer and granulator is first dedusted in cyclones, and then sent to the same gas scrubber used for scrubbing the off-gas from the CN-conversion section.

Dry granules are screened over double-deck screens. Fines, crushed oversize, and part of the on size are returned to the granulator. A two-stage fluidized bed cooler, of which the second stage is operated with chilled and conditioned air, cools the product to the desired final temperature. The waste air from the fluidized bed cooler must be treated to remove dust.

Coating takes place in a rotating coating drum to improve product characteristics during storage. From the coating drum, product is sent to storage.

The BASF granulation process for CAN can use either “AN-wet” lime – lime from the lime filter, which is washed with AN solution, or dry lime, which is water-
washed lime. For either alternative the residual water content of the AN-melt must be adjusted.

The advantage of using “AN-wet” lime is that a considerable amount of energy and capital is saved. A saving of energy occurs because no dilution of AN-solution with wash-water occurs and no lime drying takes place. Investment is reduced because lime drying equipment is not required.

In prilling CAN, the AN solution is premixed with dry lime immediately before prilling. A rotating, perforated bucket is the preferred type of drop-forming apparatus. Prill towers for both CAN and AN commonly are 45-56 m high although shorter ones are also used. For high-density prilling using 99.7% solution, prilling towers that are 15-30 m tall may be used. Cooling may be conducted in a rotary cooler or in a fluidized bed either in the bottom of the prill tower or in a separate unit.