The Technology and Economics of Dicalcium Phosphate via Nitric Acid Cycle

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D URING the past several years, Nossen Laboratories has been working on a new process to make dicalcium phosphate. The approach combines older techniques, such as nitric acid acidulation of phosphate rock, with some new ideas. Two unique aspects are a nitric acid recycle and well defined conditions for decomposing calcium nitrate. Pilot plant data indicate that both fertilizer and feed-grade dicalcium phosphate can be made by the new process, with plant investment markedly lower than that required for conventional plants.

The first attempts to use nitric acid as an acidulating agent for phosphate rock, some 50 years ago, are recorded in the patents of Brettville (2), Braun (1), and Schlutius (10). While the production of two plant food ingredients (N and P_2O_5) in one operation seemed to be a distinct advantage, the physical nature of the products (such as their extreme hygroscopicity) made them unsuitable for fertilizer use.

Much work has since been done to overcome this drawback. A suitable complex fertilizer is formed by converting calcium nitrate wholly or partially into ammonium nitrate and potassium nitrate by ammoniating acidulated rock and adding potassium sulfate to the ammoniated product, as described by Quanquin of France (9).

A different approach has been made in Holland by Plusje (8). Part of the calcium nitrate formed in rock acidulation is separated by crystallization; the mother liquor is then ammoniated to produce a mixture of dicalcium phosphate and ammonium nitrate.

Dicalcium phosphate is also a product in the reaction schemes proposed by Hignett (5) using nitric acid for acidulation and ammonia for precipitation. In one of his proposals the calcium nitrate, after separation from the phosphorus compound, is combined with ammonium carbonate to form ammonium nitrate and calcium carbonate.

Acidulation of phosphate rock with nitric acid is now commercially applied in several plants, both in the United States and abroad, for the production of complex fertilizers. But it is doubtful that this process will replace conventional methods for making superphosphate and triple super.

The fact that dicalcium phosphate in mixed fertilizer is soluble in citrate but not in water should not be a hindrance, since in ammoniated fertilizer mixtures the monophosphate is also converted into dicalcium phosphate. Probably more than one-third of the phosphate used as fertilizer reaches the soil as dicalcium phosphate.

Plant experiments show that the cumulative harvest from dicalcium phosphate fertilized soil is about the same as that from soil treated with monocalcium phosphate. The first harvest, though, is usually greater using monocalcium phosphate. It is probable that plant experiments extending over 3 to 5 years would show dicalcium phosphate to be superior, because water does not wash it out of the soil.

Production of complex fertilizers requires a large nitric acid plant and an expensive ammonia plant. But ammonia production is not always feasible in places where phosphorus rock can be most favorably converted into a plant feed. Only a few companies working in the phosphorus field are also in the nitrogen field, and vice versa. Plant capacity now in place for nitrogen fertilizers is sufficient for

NITRIC ACID CYCLE FOR PRODUCTION OF DICALCIUM PHOSPHATE
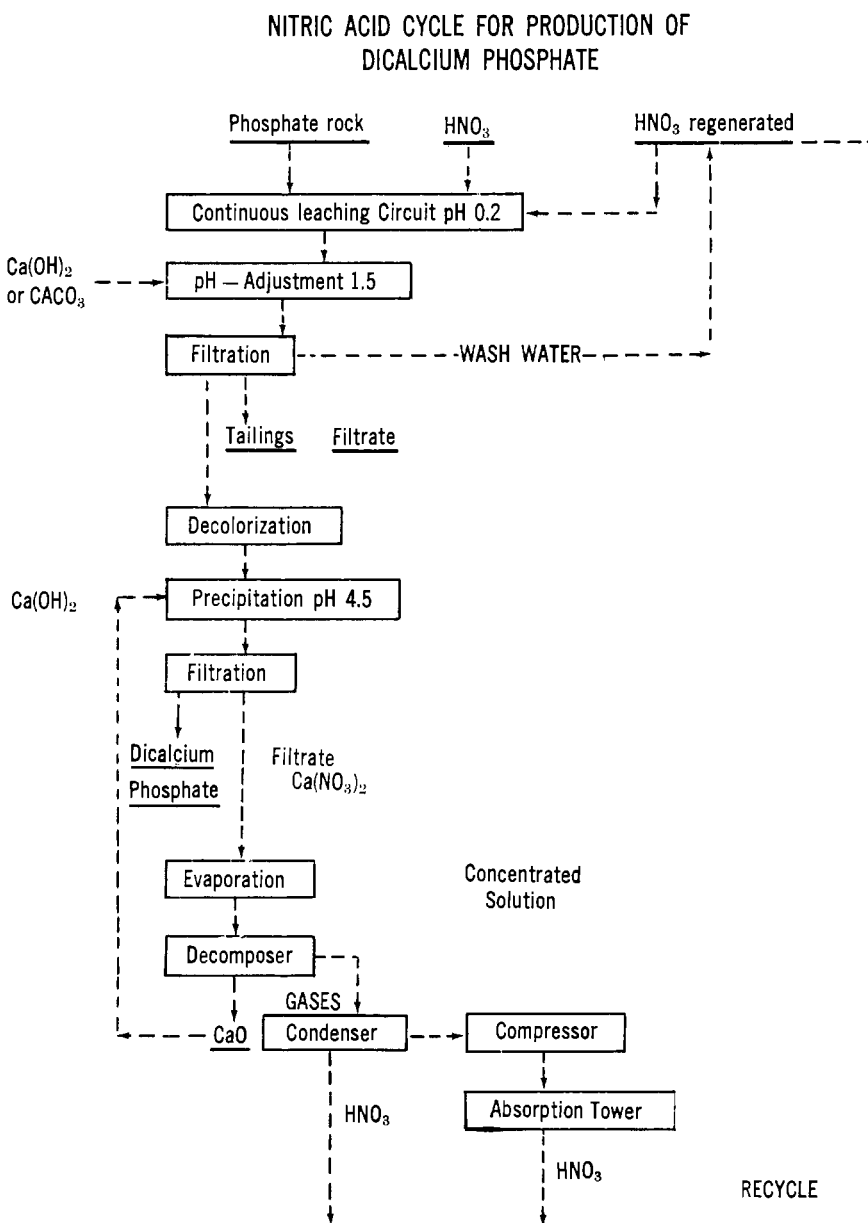
a number of years. Finally, the investment required for a plant to produce complex fertilizers with 50,000 tons P_2O_5 a year is over $20 million, or at least $400 per annual ton P_2O_5. A superphosphate plant of equal P_2O_5 production and including a sulfuric acid plant costs about $4 million, or $80 per annual ton P_2O_5.

In the nitric acid cycle developed by Nossen Laboratories for treatment of phosphate rock, the rock is first acidulated with nitric acid in the known manner; phosphorus compounds, either as phosphoric acid or monocalcium phosphate, and calcium nitrate in solution are separated by lime precipitation to give crystalline dicalcium phosphate and a calcium nitrate solution. This solution is concentrated in an evaporator and thermally decomposed into solid lime and a gas from which the nitric acid is recovered by condensation and absorption. Both decomposition products are recycled—the acid for acidulating fresh rock, and the lime for precipitating dicalcium phosphate. Some excess lime becomes available for sale. The idea of the cycle and the development of conditions for decomposition of calcium nitrate are the novel features of this process.

The nitric acid cycle was originally developed for the extraction and concentration of metals from low-grade ores (6). It has been successfully pilot-planted on a scale of 12 tons of manganese ore per day. This large-scale operation confirmed data from semipilot plant tests, and delivered additional data valuable in engineering a commercial plant (4).

Success of the nitric acid cycle hinges on two factors: complete and smooth decomposition of the metal nitrate; and efficient nitric acid recovery.

Metal nitrates other than those which form nitrites develop thick brown fumes of NO_2 when heated in a dry state. If the metal nitrate is heated above its decomposition point in a boat inside a glass pipe while sufficient steam is led over the boat, no brown fumes appear. Nitric acid, which can be collected and titrated, is formed instead.

From this discovery (7) made several years ago, it was concluded that unstable N_2O_5 is the primary decomposition product. The anhydride reacts readily with water to form the acid in vapor form, which can be condensed. Decomposition of the oxide N_2O_5 is retarded by the presence of oxygen in the decomposition, while an excess of water stabilizes the formed HNO_3 in the hot zone. Fast removal and chilling of the gaseous reaction products is further essential to obtain maximum HNO_3 directly from the condenser.

The noncondensable gases NO_2 and NO are absorbed from the gas stream in an absorption system. Their quantity relative to the condensed acid depends on the temperature and speed of the decomposition reaction. For example, manganese nitrate decomposing instantaneously at 180° C. delivers 90% of the acid in liquid form; calcium nitrate decomposed at 650° gives over 50% of its acid directly from the condenser.

In practice, instead of using dry salts and steam, concentrated salt solutions are decomposed continuously, avoiding crystallization and separation of metal nitrates. Rapid and complete decomposition is favored by having the salt solution spread in a thin film over a large surface. This is accomplished by spreading it over a metallic or mineral surface heated to a temperature above the decomposition point. If the decomposition of the metal salt proceeds so rapidly that it takes only a fraction of a minute, as with manganese nitrate, an internally heated drum makes a very suitable decomposition reactor. Decomposition takes place on the surface of the drum.
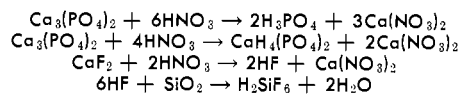
Calcium nitrate, however, requires a decomposition time of 15 to 20 minutes and a temperature of about 650° C. Hence the drum decomposer is not suitable; instead, calcium nitrate is decomposed at the surface of granular mineral particles, which are themselves not affected by the decomposition conditions. The particles can be fed to and discharged from any type of reactor so long as allowance is made for the required retention time and temperature. An externally heated rotary kiln has been successfully applied to this reaction. Part of the discharged lime is recycled and serves as a carrier for fresh salt solution.

Table I. Dicalcium Phosphate, Fertilizer Grade (36% P_2O_5)

INVESTMENT: $4,500,000.00
  For: Phosphate-plant, nitric acid recovery and make-up acid unit

PRODUCT: 394 tons/day = 14,200 units P_2O_5
FEED: 450 tons/day
DAILY OPERATING COST:

RAW MATERIALS: Phosphate rock 450 tons @ $5.15/ton	$2318.00
Limestone 125 tons @ $2.00/ton	250.00
Nitric acid (make-up) 25 tons @ $40.00/ton	1000.00
UTILITIES: Fuel 5000 × 10⁶ B.t.u. @ $0.35/10⁶ B.t.u.	1750.00
Power 40,000 k.w.h. @ $.01/k.w.h.	400.00
Water	60.00
LABOR: Operators and helpers (192 man hr.)	442.00
Maintenance (64 man hr.)	147.00
Supervision (32 man hr.)	112.00
OTHER EXPENSES: Supplies	80.00
Taxes, insurance	120.00
Plant overhead	360.00
DEPRECIATION: 10% per year of $4,500,000.00, per day	1350.00
	8389.00
CREDIT: For 120 tons lime @ $10.00	1200.00
Factory cost for 14,200 units P_2O_5:	$7189.00

Per Unit: 50.6 cents

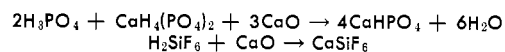## Table II. Dicalcium Phosphate Feed Grade (45% P_2O_5)

INVESTMENT: $4,500,000.00
  For: Phosphate plant, nitric acid recovery and make-up acid unit

PRODUCT: 300 short tons/day
FEED: 450 tons/day
DAILY OPERATING COST:

RAW MATERIALS: Phosphate rock 450 tons @ $5.15/ton	$2318.00
Limestone 125 tons @ $2.00/ton	250.00
Nitric acid (make-up) 25 tons @ $40.00/ton	1000.00
Activated carbon	750.00
UTILITIES: Fuel 5000 × 10⁶ B.t.u. @ $0.35/10⁶ B.t.u.	1750.00
Power 40,000 k.w.h. @ $.01/k.w.h.	400.00
Water	80.00
LABOR: Operators and helpers (192 man hr.)	442.00
Supervision (48 man hr.)	168.00
Maintenance (64 man hr.)	147.00
OTHER EXPENSES: Supplies	100.00
Taxes, insurance	120.00
Plant overhead	360.00
Bags	800.00
DEPRECIATION: 10% per year of $4,500,000.00, per day	1350.00
	10,035.00
CREDIT: For by-products at cost:	
120 tons lime @ $10.00 ($1200.00)	
135 tons fertilizer @ $7.50 ($1010.00)	2210.00
Total factory cost for 300 tons:	$7825.00

Per ton: $26.08
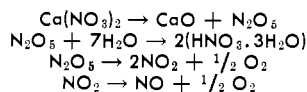
Main Reactions in the Nitric Acid Cycle

Acidulating

$$Ca_3(PO_4)_2 + 6HNO_3 \rightarrow 2H_3PO_4 + 3Ca(NO_3)_2$$
$$Ca_3(PO_4)_2 + 4HNO_3 \rightarrow CaH_4(PO_4)_2 + 2Ca(NO_3)_2$$
$$CaF_2 + 2HNO_3 \rightarrow 2HF + Ca(NO_3)_2$$
$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

Dicalcium Phosphate Precipitation

$$2H_3PO_4 + CaH_4(PO_4)_2 + 3CaO \rightarrow 4CaHPO_4 + 6H_2O$$
$$H_2SiF_6 + CaO \rightarrow CaSiF_6$$

Decomposition of Calcium Nitrate

$$Ca(NO_3)_2 \rightarrow CaO + N_2O_5$$
$$N_2O_5 + 7H_2O \rightarrow 2(HNO_3 . 3H_2O)$$
$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$
$$NO_2 \rightarrow NO + \tfrac{1}{2}O_2$$

In the process, calcium nitrate solution is sprayed into a fluidized bed initially filled with calcium oxide particles. Decomposition proceeds, and calcium oxide is removed from the bottom of the reactor at the same rate that it forms on the particles from the nitrate solution. Heated steam or air is used as fluidizing agent; the reactor is heated mainly through the walls from the outside.

Gaseous decomposition products are passed through a condenser, from which most of the nitrogen is recovered as liquid acid. Non-condensables are compressed in a pressurized tower, where the nitric oxides are converted to nitric acid with an efficiency of 97%. Since the solid decomposition product, calcium oxide, can be controlled at 0.02% N, and 50% of the acid is recovered directly from the condenser without loss, nitric acid loss in decomposition is less than 2% of the total acid applied. Another 1% or so is retained in the dicalcium phosphate (3).

The nitric acid cycle flowsheet is very simple and straightforward. Leaching can be done in continuous operation requiring about 30 minutes for 95% P_2O_5 recovery in leach solution. Separation of phosphorus compound from calcium nitrate is completed at a pH of about 4.5. Because of its crystalline structure, the dicalcium phosphate is easily filtered, washed, and dried.

Calcium nitrate solution is concentrated from 38% to 75% in an evaporator. The concentrated solution is decomposed in an externally heated rotary kiln or in a fluidized bed reactor. Nitric acid (45%) is recycled to the leaching step, and part of the calcium oxide to the precipitation step. Since calcium oxide is more expensive than limestone, it may be more economical to sell the oxide and at least partially replace it in the precipitation with limestone.

The flowsheet shows two purification steps required in the production of feed grade dicalcium phosphate. At pH 1.5, iron, aluminum, and the greater part of fluorine are removed with limestone or lime, together with the gangue. The precipitate contains 12% to 15% P_2O_5 and 24% CaF_2 which could be used to make fluorine compounds, or in fertilizer mixtures. The original leach solution contains 75% of the total fluorine content of the rock. At pH 1.5, 97% of the fluorine content of the rock is removed from the solution. The nitrate solution at pH 4.5 is free from fluorine. A material balance shows that hardly any fluorine is released as a gas.

The filtrate is decolorized prior to dicalcium phosphate precipitation. Feed grade dicalcium phosphate has been produced with the following analysis: P_2O_5—46.0%, F—0.17%, N_2—0.21%, and CaO—41.7%. 1000 lb. of rock with 33% P_2O_5 furnished 870 lb. of fertilizer grade dicalcium phosphate with 36% P_2O_5, or 615 lb. of feedgrade dicalcium phosphate with 46% P_2O_5, besides 265 lb. of the fluorine-containing fertilizer coproduct.

Fertilizer and feedgrade materials are produced alternately in the same installation according to seasonal demands.

The total cycle takes less than two hours and requires relatively small pieces of equipment and a low investment for a plant of large capacity. The process is applicable to low-grade rocks, producing from them products identical with those made from standard raw material.

Process data obtained in semipilot plant trials have been scaled up to a projected commercial operation handling 450 tons of rock a day. With the experience and data obtained from the larger pilot plant using the nitric acid cycle, and quotations obtained from equipment manufacturers, investment and processing costs have been estimated. Fuel and power requirements have been calculated and checked against comparable pilot plant data.

The investment is about the same as for a wet phosphoric acid plant with the required sulfuric acid plant. Make-up nitric acid is produced at the plant by an ammonia burner integrated with the acid recovery system. The calculation allows for nitric acid losses of 5% of daily throughput, almost double the loss actually encountered.

The cost of the product depends upon the cost of rock and fuel, which together account for 50 to 60% of the total cost. Therefore it is not possible to give a specific figure. But calculations made under different price conditions for these commodities indicate that a fertilizer grade dicalcium phosphate can be produced at a cost of 47 to 53 cents per unit, and feed grade product at $25 to $30 per short ton.

Table I gives a breakdown of the factory cost for fertilizer grade dicalcium phosphate. The figure of 50.6 cents per unit of P_2O_5 compares very favorably with superphosphate's cost of about 65 cents per unit.

Table II gives a breakdown of the factory cost for feed grade material—$26.08 per ton. Under comparable production conditions, the factory cost per ton of feed grade dicalcium phosphate would be: by superphosphate leaching and precipitation, $44.00; by neutralization of wet phosphoric acid, $48.00; by neutralization of furnace acid, $54.00.

This cost comparison shows that the nitric acid cycle substantially cuts production cost of phosphate products through the recovery of acid and lime. In addition, natural resources of sulfur and lime are conserved for future use.

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