Ammonium Phosphates via Wet Process Acid

A close look at how the competitive processes for using wet process acid to make ammonium phosphates compare—both technically and economically

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As PART OF the current trend toward production of complex, high analysis fertilizers, interest in fertilizer grade mono-(11-48-0) and di-(18-48-0) ammonium phosphates has reached an all-time high. Three new plants have started up during the last year, and four more are in the construction stage. The increased interest is due largely to:

Recognition of the advantages of a concentrated product relative to storage, freight, and handling costs.

Advances in manufacturing technology.

Expectations of a glut in anhydrous ammonia supplies in 1957.

Widespread consumer education relative to the ammonium phosphates on the part of manufacturers and state agricultural agencies.

A variety of commercial processes, combining the wet process for phosphoric acid with means for producing the ammonium phosphates, have become available and will be vying for greater attention in the future. In each, the fundamental chemistry is the same. By acidulating phosphate rock, phosphoric acid containing residual amounts of sulfuric acid is obtained and neutralized with ammonia to mono- or di-ammonium phosphate. How the MAP and/or DAP is recovered from the resulting slurry varies with the process. Here is a close look at how the competitive processes compare, both technically and economically.

Wet Process vs. Furnace Grade Phosphoric Acid

There are two general methods used for the manufacture of phosphoric acid. In the first, known as the wet process, phosphate rock is treated with sufficient sulfuric acid to convert the P_2O_5 content completely into orthophosphoric acid. An insoluble residue, largely calcium sulfate (gypsum), is filtered off. The acid produced is saturated with gypsum, and contains other impurities introduced with the rock.

The second is the furnace method in which phosphate rock is fused in the presence of reducing materials. Elemental phosphorus is produced and burned with air to form P_2O_5. This is absorbed in water to give an acid of high and uniform purity.

In general, and under prevailing economic conditions, it is substantially cheaper to make phosphoric acid by the wet process than by the thermal reduction process. Under special circumstances, however, furnace grade acid may be preferred. For example, at two of the four plants now under construction plans are to use furnace grade acid until the level of production justifies investment in wet process facilities.

The Wet Process

It is common practice to identify a wet acid process by the type of gypsum crystal formed during acidulation, that is, dihydrate, hemihydrate, or anhydrite. The dihydrate process is commonly used today primarily because of the ease with which the crystals form.

Research continues on the hemihydrate and anhydrite processes with their promise of higher product acid strength which would result from the more readily filterable nature of the crystals produced. The major obstacle to their commercial application has been the high acidulation temperatures and acid strengths required to assure crystal stability. The required conditions present problems in control and materials of construction that have discouraged plant designers, although the construction of a plant in Italy using the anhydrite process was recently announced.

The principal reaction in the dihydrate process is between the rock (primarily fluorapatite, $3Ca_3(PO_4)_2 \cdot CaF_2$) and sulfuric acid to give phosphoric acid and calcium sulfate. The reaction actually takes place in two stages. In the first, tricalcium phosphate is converted, in the presence of a large excess of phosphoric acid, into soluble monocalcium phosphate. In the second, the monocalcium phosphate reacts with the sulfuric acid, precipitating calcium sulfate as the dihydrate.

The key to success in any wet phosphoric acid process lies in the control and operation of the reaction station. If the conditions selected here are proper, the subsequent steps of filtration and, where required, evaporation, become simple chemical engineering operations. In carrying out the reaction, the objectives are: (1) to obtain maximum extraction of P_2O_5, and (2) to produce an easily filterable and washable calcium sulfate so that there will be a minimum loss of soluble P_2O_5 in the waste.

Those reaction variables subject to control by the designer and/or operator, and of significance in attaining the stated objectives are:

Particle size of the phosphate rock.
Retention time in the digesters.
Sulfate ion concentration in the reaction slurry.
Sulfuric acid concentration.
Reaction temperature.
Recycle ratio of unseparated reaction products.

Figure 2. The Dorr-Oliver traveling pan filter
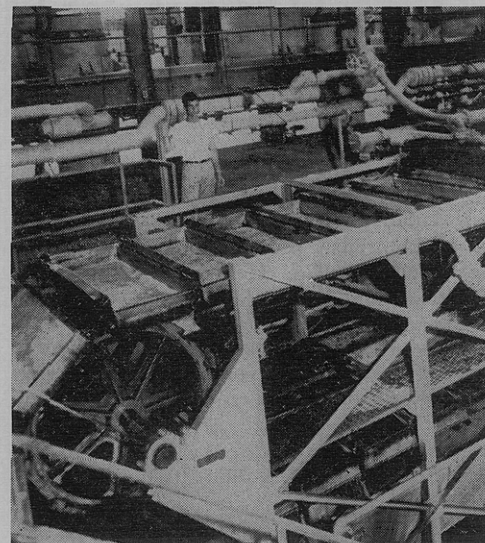
The rock must be ground fine enough to permit complete extraction of the P_2O_5 in the retention time allowed. Special provisions for agitation and acid addition in the digesters also influence the fineness required, and help control the sulfate ion concentration. If the latter becomes too great at any point in the system, precipitation of gypsum becomes so rapid at the rock-acid interface that the particles are coated with gypsum before the P_2O_5 is completely extracted.

The strength of sulfuric acid employed is important to both filter cake washing and heat considerations. There are two points of water entry: with the sulfuric acid, and as wash water to the filters. In order to produce a given quantity of phosphoric acid of a specified strength, the total water requirements are fixed. Such being the case, the concentration of sulfuric acid used determines the amount of fresh filter wash that can be employed as well as the extent to which auxiliary means of cooling the reaction slurry must be provided.

Maintenance of the proper reaction temperature is of paramount importance to the wet process, particularly when product acid strengths greater than 30% P_2O_5 are desired. The reaction temperature must be high enough to promote efficient P_2O_5 extraction from the rock and yet low enough to permit stable dihydrate crystal formation.

It has been found desirable to maintain a large recycle of unseparated reaction products leaving the digestion system. When this stream is added with the materials entering the system it acts as a diluent to control the sulfate ion concentration. It also serves as a source of existing crystal surface, discouraging the formation of new crystal nuclei and permitting the growth of large, easily filterable and washable crystals.

Assuming the production of a desirable gypsum slurry, its filtration resolves itself to the selection of the most appropriate of several continuous vacuum filters available today. These are the Mercer-Robinson band filter, the Dorr-Oliver horizontal rotary filter, the Dorr-Oliver (Giorgini) traveling pan filter, and the Bird Prayon and Eimco horizontal rotary tilting tray filters.

All the filters boast rugged mechanical design features, giving minimum wear and replacement of parts. They are essentially similar in principle but vary in mechanical design. The main features used for comparison are the materials of construction, filtration efficiency, cake and cloth washing efficiency, frequency and ease of filter
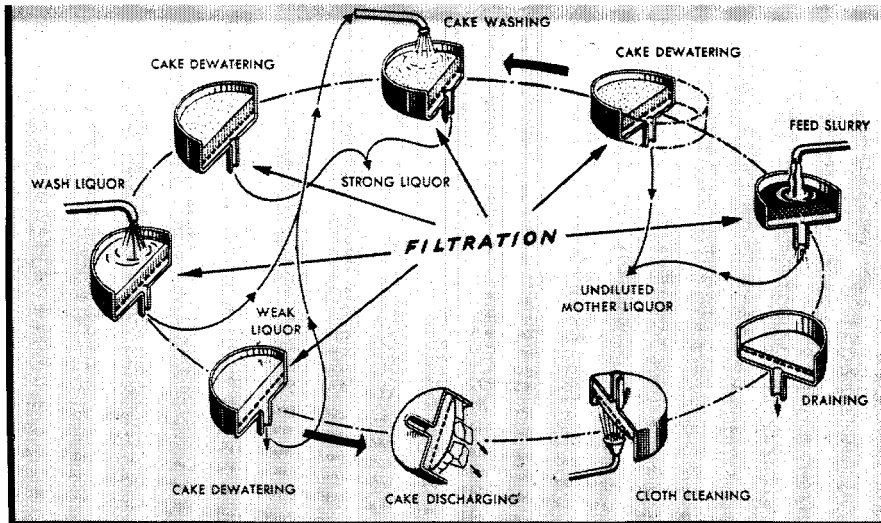

Figure 1.   The operating cycle of the Bird Prayon filter

cloth replacement, floor space requirements, preference for single or multiple units, and installed cost.

Figure 1 shows the operating cycle of the Bird Prayon filter. Its cycle is typical of all the filters and consists essentially of five operations:

Separation of the product acid from the gypsum.

Washing of the resultant cake using filtrate from the final wash.

Washing of the cake using heated fresh wash.

Removal of the cake from the cloth.

Washing of the cloth preparatory to receiving fresh slurry.

The filtrate from the primary wash is recycled to the reaction station.

The Dorr-Oliver traveling pan filter is shown in Figure 2. Preference in the newer plants has been for this type or the horizontal rotary tilting tray filters.

Whether or not concentration of the acid by evaporation is required is dependent upon the remainder of the process. Water may be removed from the acid by evaporation and/or from the ammonium phosphates by drying during the granulation process. The choice becomes one of economics and ease of operation. With wet acid of 30% P_2O_5 content or higher, the latter alternative is usually preferred.

Ammonium Phosphate Production

Conversion of the phosphoric acid to the ammonium phosphates would be a simple matter if it were not for the impurities present. These vary with the composition of the rock used in the manufacture of the acid but are primarily iron, aluminum, sulfate, and fluoride. Treatment of the acid with ammonia in the neutralizers results in almost complete precipitation of the iron and aluminum as complex orthophosphates, and partial precipitation of the sulfates and fluorides. The product is a thick slurry or crystal magma.

A granulated product is produced from the neutralized slurry in all processes available today except that of TVA which employs crystallization. In granulation, the slurry is mixed with a large quantity of previously produced undersized granules in such a way that the granules are given a thin uniform surface coating of wet slurry. Depending upon the amount of undersize recycled, the process may be one of layering or particle agglomeration. The latter permits the use of a lower recycle ratio at some sacrifice in particle uniformity.

The moistened product is dried, usually in concurrent, direct heat, rotary driers, and closely sized in double deck vibrating screens. The oversize is pulverized and returned with the fines to the mixer. The drier gases, before release to the atmosphere, are water washed for removal of any fine dust and fluosilicates.

The number of tons of recycled fines required per ton of product depends upon the water content of the slurry and the product particle size desired. Most producers feel that a 6 to 10 mesh product is preferable. When necessary a portion of the product stream is ground with the oversize to increase the amount of recycle. From the screens the material in the desired size range is conveyed to bulk storage from which it is reclaimed for bagging.

Four commercial processes for the manufacture of wet process acid and its conversion to the ammonium phosphates are being offered today. These are in addition to the TVA process for the latter step only. Know-how on manufacture of the acid alone is available from numerous sources other than those considered here. The most recent is Davison Chemical Co. with its clinker process, in which 50% P_2O_5 acid is leached in high yield from a clinker formed by heating freshly acidulated rock.
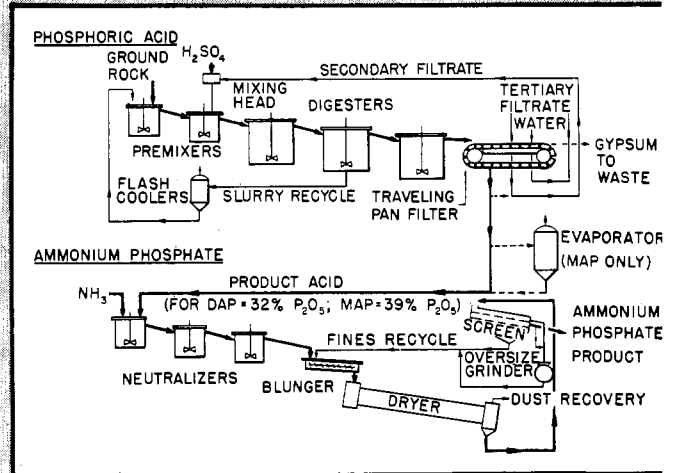
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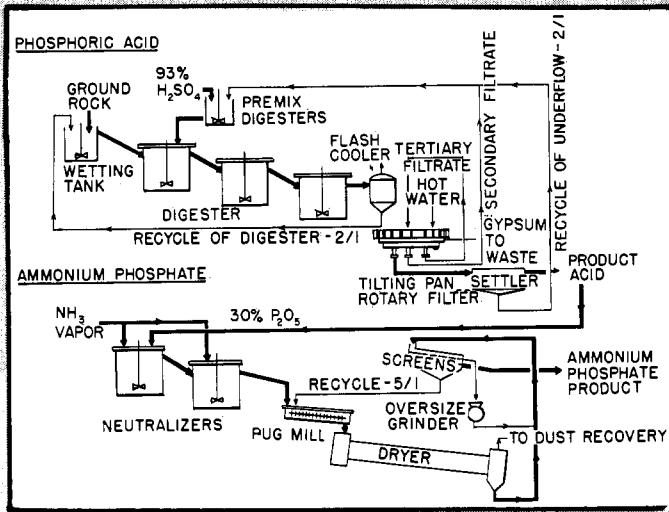
◀ Fig. 3 Chemico Process

Fig. 4 Dorr-Oliver Process ▶

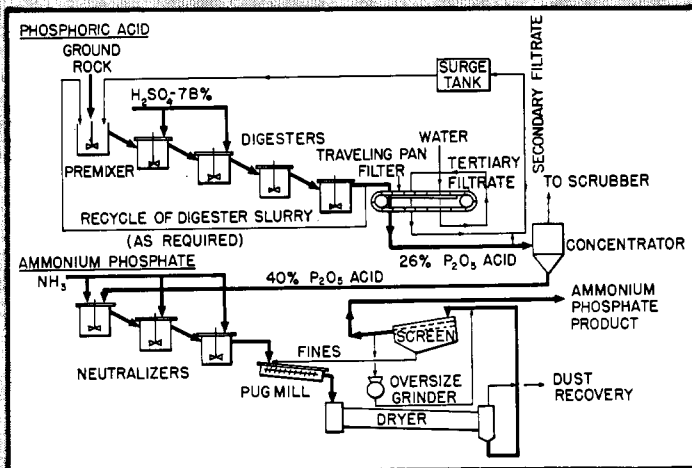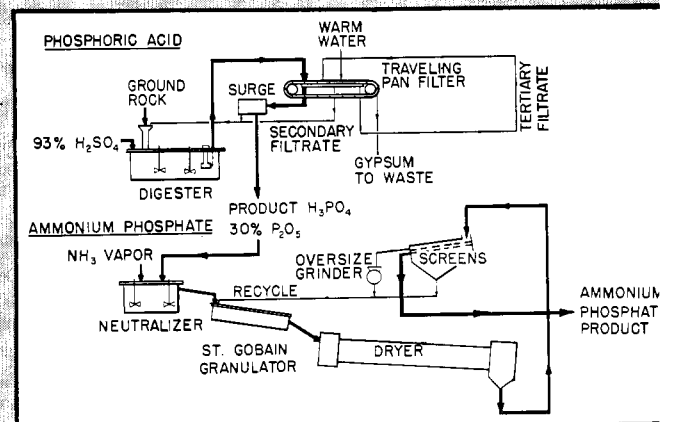**◀ Fig. 5 Knowles Associates Process**

Fig. 6 Fluor Process ▶
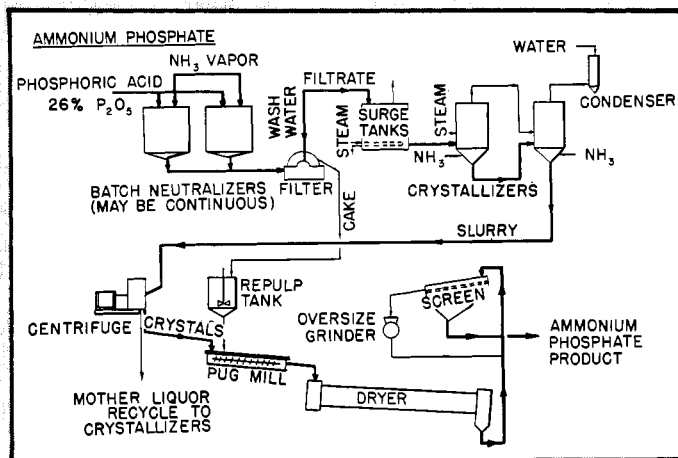
mmonium Phosphates

Fig. 7. TVA Process

Chemico (Figure 3)

Ground rock is slurried in a wetting tank with recycled digester slurry and the combined stream is allowed to flow through three digesters in series. Sulfuric acid, secondary filtrate, and product acid settler underflow are premixed and added in the first digester; reacted slurry leaves the third to be filtered. The product acid (filtrate) goes to a settler where fines are separated and recycled with the underflow. Neutralization is carried out in two tanks in series and the resulting slurry is fed to a twin shaft pug mill for granulation. Drying and screening are handled conventionally.

SPECIAL FEATURES: Use of submerged coils and flash cooling for close control of digestion temperature. Low recycle of digester slurry in acid plant and of fines during granulation in MAP plant. Recovery of dust from hot gases leaving the dryer, by recycling MAP solution through a wet collection system. Recovery of ammonia from neutralizer fumes by scrubbing with dilute H_2SO_4.

Dorr-Oliver (Figure 4)

Ground rock and cooled, recirculated slurry from the second of three digesters are brought together in the first of two premixers; mixed sulfuric acid and recycled weak acid are added in the second. The combined stream flows by gravity through the premixers and digesters in series and the final reacted slurry is then filtered. The product acid (filtrate) is neutralized in three tanks operated in series and the resulting slurry is granulated in a

blunger. Drying and screening operations are conventional.

SPECIAL FEATURES: Use of sparged air and flash cooling of the slurry to obtain close temperature control in the digesters. Production of high strength (32% P_2O_5) acid directly from the filters. Recovery (for return to process) of dust in dryer exit gas stream and of ammonia from neutralizer fumes using patented Doyle scrubber. Granulation designed to produce a smooth, nearly spherical product.

Knowles Associates (Figure 5)

Ground rock is premixed with secondary filtrate and recycled digester slurry (as required to maintain proper sulfate ion concentration) and allowed to flow through four digesters in series. Sulfuric acid is added in the first two digesters. The reacted slurry is filtered, and the product acid brought to 40% P_2O_5 in a submerged combustion-type concentrator. Neutralization is carried out in three tanks in series and the resulting slurry is granulated with recycled fines in a pug mill. Drying and screening are handled conventionally.

SPECIAL FEATURES: Digestion temperature closely controlled using water-jacketed digesters, diluted and precooled sulfuric acid, and low pressure air flow in the digesters. Low recycle of digester slurry in acid plant. Recovery of dust from dryer gases by recycling MAP solution through wet scrubbing system.

Fluor (Saint-Gobain) (Figure 6)

Ground rock, sulfuric acid, and secondary filtrate, plus some prod-

uct acid, are fed to a large, well-agitated digester. The resulting slurry is withdrawn continuously by means of a vertical submerged pump and sent to a traveling pan vacuum filter. The product acid (filtrate) is neutralized in a single tank and the effluent combined with dried recycle material in the specially designed St. Gobain granulator (details confidential). Drying and screening are conventional.

SPECIAL FEATURES: Digestion system will use rock with a relatively coarse grind; 40 to 60 mesh is usually sufficient. No slurry recycle is required in the acid plant. Acid plant may be started and stopped at will permitting less than 24-hour-per-day operation.

TVA (Figure 7)

Wet process acid is neutralized to the proper pH and the resultant precipitate (principally complex iron and aluminum orthophosphates) is separated by filtration. The filtrate and additional ammonia are fed to continuous vacuum crystallizers. The ammonium phosphate crystals are separated from the magma in continuous centrifuges and the mother liquor is recycled to the process. The crystals and repulped filter cake (it is thixotropic) are mixed in a pug mill, dried and screened. Most of the product is between 6 and 60 mesh.

SPECIAL FEATURES: Can use low-strength phosphoric acid. Produces a high purity crystalline product. Utilizes portion of heat of neutralization as source of heat in crystallizers. Only surface moisture must be removed by drying and no recycle of fines is required.

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the joint venture which resulted in
construction of Northwest Nitrochem-
icals' fertilizer plant in Canada.

the way to the ammonium phosphates
are offered by:

Chemical Construction Corp.
(Chemico)
Dorr-Oliver, Inc.
Fluor, Ltd. (St. Gobain process)
Knowles Associates

Chemical & Industrial Corp. offers
the Prayon process for the manufac-
ture of wet process acid and the PEC
nitric acidulation complex fertilizer
process. A PEC plant can produce
ammonium phosphate but is not rec-
ommended where the latter is the
principal product. Use of the St.
Gobain process offered by Fluor re-
quires a royalty which may be as-

sessed on actual production or paid
as a lump sum based on plant capacity.
The four processes listed here
differ primarily in the rock digestion,
acid slurry filtration, and acid neu-
tralization steps. A brief description,
a simplified flowsheet, and a listing of
special features is presented for each
of these processes as well as that de-
veloped by TVA in Figures 3, 4, 5, 6,
and 7 (see pages 260 and 261).
Table I presents a summary of the
raw material, utility, and labor re-
quirements for three of the commer-
cial processes. These data as well as
those presented in Tables II and III
are based on a plant capable of pro-
ducing 250 tons per 24 hour day of
MAP (11-48-0) in the bag. This
corresponds to 120 tons per day of
P_2O_5.
The lime required in the phosphoric
acid plant is for neutralization of a
composite waste stream made up of
gypsum slurry, fume scrubber liquor,
and other acid containing wastes.
One of the most important aspects of
wet process plant site selection is
consideration of the effluent problem.
MAP production cost estimates cor-
responding to the data in Table I are
shown in Table II. The battery limits
plant[1] for which these data apply,
includes rock grinding, in-process
storage, all equipment, motors and
motor control centers, instruments and
controls, bagging, and buildings and
foundations—all erected to include
contractor's overhead and fee. Not
included are plant site, railroads, of-
fices, product storage, and auxiliary
facilities for services and utilities.
Ammonia and sulfuric acid have
been entered at sale price rather than
production cost since the latter varies
with the producer. The usual pro-

duction costs for ammonia and sul-
furic acid are $42 to $45 and $11 to
$13 respectively. By comparing the
total manufacturing costs in Table II
with the current selling price for MAP
of $95 f.o.b. plant, it is apparent that
a producer should have captive
sources of these two raw materials.
The same is true to a lesser degree of
the phosphate rock.
It is interesting to note that while
the individual energy requirements
shown in Table I vary considerably
between processes, cost of the total
requirements, when determined on a
per ton basis from Table II, are nearly
identical. This is true whether excess
moisture is removed by a combination
of evaporation from the acid and dry-
ing of the final product, or by drying
alone.
On paper one process may look
best, but field conditions relating to
the availability of raw materials or
utilities, type of construction required,
integration into other operations, flexi-
bility, or other considerations might
well give another the edge in a spe-
cific case. For any proposed installa-
tion, each process should be carefully
evaluated to determine what advan-
tages it may offer.

Diammonium Phosphate

To produce diammonium phos-
phate, ammonia concentrations must
be higher than those needed for MAP,
causing increased losses of ammonia
from the neutralizers. DAP is also
more heat sensitive and additional am-
monia is lost during drying. Until re-
cently, the need for recovering these
losses has discouraged producers of
mono from entering the diammonium
market.
Dorr-Oliver is now offering a proc-
ess, proved in a commercial plant, for
producing a 20–80 mixture of mono
and diammonium phosphate. Am-
monia losses are kept down by use
of a two-stage neutralization in which
the free ammonia concentration nec-
essary is reduced by ammoniating first
to mono and then to di, and by selec-
tion of the proper phosphoric acid–
ammonia mole ratio and solution con-
centration to give the minimum am-
monia partial pressure.
Ammonia that is lost from the neu-
tralizers and dryer is recovered in an
impingement scrubber and returned
to the process. Except for the evapo-
ration system, Dorr-Oliver uses the
same equipment for producing mono
and di. In the latter, 32% P_2O_5 acid
can be used as produced without
concentration.

Table I. Raw Material, Utility, and Labor Requirements for Plant to Produce 250 T/D of MAP (11–48–0)[a]

Item	Process A		Process B		Process C	
	H_3PO_4	MAP	H_3PO_4	MAP	H_3PO_4	MAP
Phosphate rock, dry, 32% P_2O_5, T/D	400	...	403	...	398	...
Sulfuric acid, 100% H_2SO_4, T/D	340[b]	...	340[b]	...	312	3.3
Ammonia, T/D	...	35.2	...	33.4	...	34.5
Lime, T/D	5	...	5[a]	...	5[a]	...
Water, M. GPD, 20° F. rise	1,800	96	2,800	30	600	...
Electric power, KWH	16,200	10,100	18,100	12,850	15,000	15,000
Natural gas, 900 B.t.u./SCF HHV, MCF/D	...	1,155	...	300	...	890
Steam, 150 psig sat., M. lb/D[c]	65	...	260	...	65[d]	...
Supervision, man hours/D	12	12	12	12	12	12
Direct Labor, man hours/D	170	144	155	175	96	120
Analytical Labor, man hours/D	18	6	18	6	18[d]	6[d]

[a] Based on 24-hour stream day
[b] Total for both units
[c] Normally surplus steam from H_2SO_4 manufacture
[d] Estimated

[1] Battery limits, a term of military origin de-
noting a specifically defined area, is commonly
used in chemical plant construction to identify
a production unit for which a contractor or
subcontractor may be responsible.

Table II. Production Cost Estimate per ton of MAP[a] (11–48–0)

Item	Process A	Process B	Process C
RAW MATERIALS			
Phosphate rock, $15.50/T	$24.88	$24.97	$24.67
Sulfuric acid, $22.35/T	30.40	30.40	27.89
Ammonia, $80.00/T	11.26	10.70	11.04
Lime, $7.50/T	0.15	0.15	0.15
Total Raw Materials	66.69	66.22	63.75
LABOR			
Supervision	0.36	0.36	0.36
Production and Analytical	3.02	3.16	2.41
Maintenance[b]	0.83	0.78	0.95
UTILITIES			
Water, $7.00 per MM gal.	0.05	0.08	0.02
Power, $0.007 per KWH	0.74	0.86	0.84
Natural gas, $0.125 per MCF	0.58	0.15	0.45
Steam, $0.40 per M lb.	0.10	0.42	0.10
SUPPLIES			
Operating	0.10	0.10	0.10
Maintenance[b]	0.83	0.78	0.95
Bags	4.00	4.00	4.00
INSURANCE AND TAXES	0.69	0.67	0.74
DEPRECIATION[c] AND ROYALTIES[d]	3.31	3.10	4.24
OFFICE AND SERVICE	1.25	1.25	1.25
Total Conversion cost	15.86	15.71	16.41
Total Manufacturing cost[e]	$82.55	$81.93	$80.16

[a] For 250 T per stream day plant; annual production based on 0.9 stream factor.
[b] Estimated as 5% of fixed capital cost per year.
[c] Straight-line method; 10% per year of cost of battery limits plant.
[d] Paid up and pro-rated over 10-year period.
[e] Present selling price: $95.00 per ton f.o.b. plant.

The costs of manufacturing MAP and the 20–80 MAP-DAP mixture using the Dorr-Oliver process are compared in Table III. The greater economy per unit of fertilizer content is evident in the case of the mixture. This advantage results from its higher analysis, since the conversion costs per ton are nearly the same.

The TVA process was originally developed for manufacture of DAP. By selecting the proper conditions for neutralization and crystallization, a fertilizer grade diammonium phosphate is obtained with an analysis of 18–47–0. Using its process, TVA has built a plant with a rated capacity of 40,000 tons per year. Furnace grade acid is used, and ammonia losses are low enough (2–3%) that recovery is not an economic necessity.

Besides being a high analysis product, DAP, like MAP, contains water-soluble P_2O_5, has a relatively low hygroscopicity and is compatible and granulates well with other fertilizer materials. Its future looks particularly promising.

Other Formulations

By varying the relative quantities of phosphoric and sulfuric acid to the neutralizers, the N to P_2O_5 ratio can be varied. This makes possible the use of the same equipment for production of such established grades as 16–20–0, 13–39–0, and 19–19–0. When potash is added during granulation, the K_2O content may be varied at will so that formulas such as 14–14–14, 14–28–14, and 12–36–12 can be produced.

The addition of nitric acid or ammonium nitrate solution to the neutralizers will permit the production of other completely water-soluble formulations, similar to these except that a portion of the nitrogen will be in the nitrate form and higher analyses are obtainable. For example, 18–18–18 could be made in place of 14–14–14.

As the number of formulations produced in a single plant increases, the scheduling and storage problems become much more complicated and costs frequently go up. Most producers specialize in those relatively few grades that are in greatest demand in their primary marketing areas.

Future Production

For the year ending June 30, 1956, according to the USDA, the average primary nutrient content of all fertilizers sold in the United States was 8.8% N, 10.1% P_2O_5, and 8.5% K_2O. These figures reflect a continuing trend toward higher $N-P_2O_5$ and $K_2O-P_2O_5$ ratios, and higher over-all nutrient content. This is largely due to the fact that farmers are becoming aware of the importance of buying fertilizers on a cost per unit of plant food rather than cost per ton basis. If this trend continues, higher analysis products such as the ammonium phosphates will assume increasing importance.

The Jan. 1, 1955, annual capacity for wet process phosphoric acid was reported by BDSA to be 993,210 tons P_2O_5, an increase of 162% over 1950. Announced new and scheduled construction since that time will raise the capacity to nearly 1.2 million tons P_2O_5 by the middle of 1957. Approximately 85% of this amount will go into fertilizers, primarily triple superphosphate and the ammonium phosphates. With the ammonia supplies available today, the ammonium phosphates promise to assume a prominent place in our fertilizer technology.

Acknowledgment

Table III. Cost Comparison for MAP vs. 20–80 MAP–DAP Mixture by the Dorr-Oliver Process

Item	MAP (11-48-0)	MAP-DAP Mixture (18-48-0)
Erected cost for 250 T/D battery limits plant	$2,540,000	$2,390,000
Raw Materials, $/T	66.22	73.03
Labor, $/T	4.30	3.98
Utilities, $/T	1.51	1.49
Supplies, $/T	4.88	4.83
Insurance and Taxes, $/T	0.67	0.64
Depreciation, $/T	3.10	2.92
Office and Service, $/T	1.25	1.25
Total Manufacturing Cost, $/T	$ 81.93	$ 88.14
Cost per unit of plant food	$1.39	$1.34