

PHOSPHATE ORE

Fertilizer from Leached-Zone Ore

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Pilot-plant development of a process for the production of fertilizer from Florida leached-zone ore—a low-grade, high-alumina phosphate ore—is described. The ore was calcined and then extracted with a mixture of nitric and sulfuric acids. After filtration, the extract was processed into fertilizer by continuous ammoniation and granulation. Typical grades of fertilizer that can be made are 15-15-15, 20-20-0, and 11-22-11. The products are well granulated, do not cake in storage, and have a satisfactory agronomic value. The process provides an opportunity for convenient recovery of uranium from ore.

FLORIDA PHOSPHATE DEPOSITS contain a layer of material called the "leached zone," in which the principal phosphate minerals are aluminum phosphates. This zone overlies the phosphate rock matrix. The leached-zone ore contains several aluminum phosphate minerals, including wavellite, pseudowavellite, and millsite, as well as calcium phosphate, similar to ordinary phosphate rock, a large proportion of silica sand, and some aluminum silicate clay (7).

The thickness of the leached zone and its composition vary widely. The prospecting data are not adequate for a reliable estimate of the quantity or average grade. Barr (2) suggests that the average thickness of the leached zone may be in the range of 5 to 15 feet and that its phosphorus pentoxide content may be 10 to 12%. He estimates that in 1954, 14,000,000 tons of leached-zone material were moved and discarded as waste in phosphate mining operations. If this material averaged 10% phosphorus pentoxide (1,400,000 tons), that would be roughly one half as much as the content of the commercial-grade phosphate rock recovered from Florida mining operations in 1954. Although these estimates do not purport to be accurate, they indicate that the leached-zone ore constitutes an important phosphate reserve. The Tennessee Valley Authority (TVA) is interested in conserving this material, which is now being wasted, by developing economical methods of producing fertilizer from it. Also, it is a potential source of uranium. Because it contains only very small amounts of uranium, the cost of processing the leached-zone ore must be borne by the fertilizer product.

In 1951, at the suggestion of the Atomic Energy Commission, TVA started work directed toward developing a means of converting this waste material into a valuable national resource.

The pilot-plant development of a nitric-sulfuric acid extraction process, which appeared the most promising for the production of fertilizer from leached-zone ore, is described briefly. A more detailed description of this work and of work on other processes for the recovery of phosphorus and aluminum from the ore is presented elsewhere (6). Studies by TVA of the beneficiation of the ore

have been described by Davenport and coworkers (3).

Pilot Plant, Nitric-Sulfuric Acid Process

A flowsheet of the process as carried out in the pilot plant is shown in Figure 1. The principal steps are:

1. Calcination of the ore at 2000° to 2100° F.
2. Extraction of the phosphorus pentoxide from the ore with nitric and sulfuric acids.
3. Filtration of the extraction slurry. (The washed filter cake, which consisted

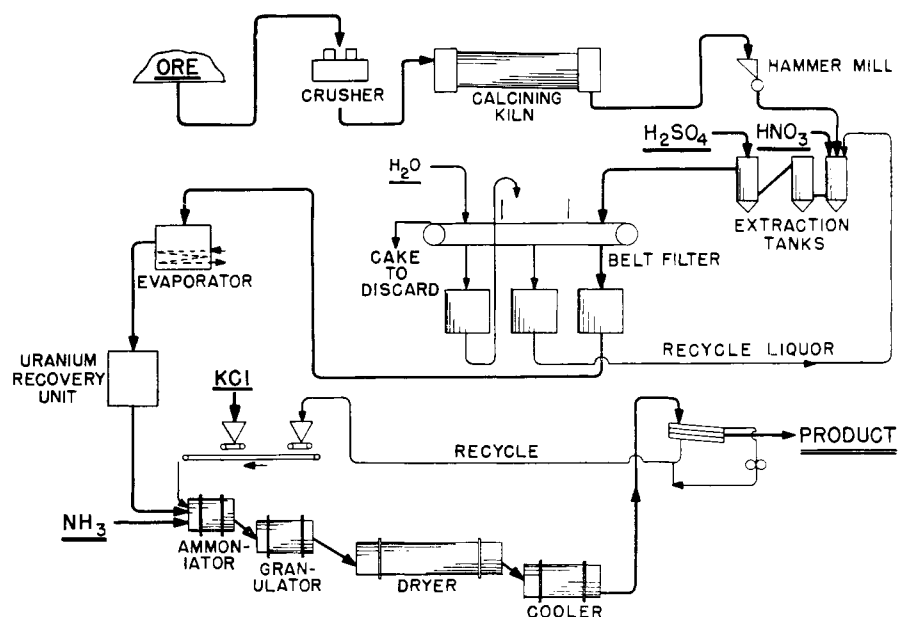


Figure 1. Flow diagram of pilot plant for production of leached-zone fertilizer

chiefly of silica sand, clay, and calcium sulfate, was discarded.)

4. Concentration of the filtrate by evaporation.

5. Ammoniation and granulation of the concentrated filtrate. (Potassium chloride was added to produce a three-component fertilizer.)

6. Drying of the product.

Most of the work was carried out with two batches of unbeneficiated leached-zone ore of the following compositions:

Ore	% by Weight (Dry Basis)						Ignition loss
	P ₂ O ₅	Al ₂ O ₃	Fe ₂ O ₃	CaO	SiO ₂	F	
V-10	15.3	10.6	3.4	11.3	51.1	1.2	6.8
V-20	9.9	8.3	1.3	7.7	65.6	0.8	5.9

A few tests showed that beneficiated ore also could be processed by the procedure used with the unbeneficiated ore.

Calcination. The ore was calcined in a gas-fired rotary kiln, 40 feet long by 2.5 feet in inside diameter, at a rate of about 1400 pounds per hour. The kiln usually was rotated at 1.6 r.p.m.; at this speed, the average time of passage through the kiln was about 50 minutes. Prior to being fed to the kiln, the ore was milled to pass a 1-inch screen to ensure more complete calcination. The tem-

perature of the ore in the hottest part of the kiln usually was held between 2000° and 2100° F. as measured by an optical pyrometer. There was little or no formation of rings in the kiln unless the temperature exceeded 2150° F. From 40 to 60% of the fluorine in the ore was volatilized during calcination.

Figure 2 shows the effects of the calcination temperature of ore V-20 on the filterability of the extraction slurry and on the extraction of phosphorus pentox-

ide and aluminum oxide (corundum). The filterability of the extraction slurry was very poor when uncalcined ore or ore calcined at 1800° F. or below was used. The highest filtration rates were obtained when the ore was calcined at about 2000° F.

Only 85% of the phosphorus pentoxide was extracted from uncalcined ore, whereas 95% or more was extracted from ore calcined at 800° to 2200° F. The proportion of the aluminum oxide extracted from the ore was a maximum

(86%) when the temperature of calcination was 1200° F. and was at a minimum (55%) when the temperature of calcination was about 2000° F. Minimum extraction of the aluminum oxide was desirable, as it would be a diluent in the fertilizer product. The filtration rate of the extraction slurry made from ore V-10 also was affected in a similar manner by the calcination temperature; about 95% of the phosphorus pentoxide and 50% of the aluminum oxide were extracted from this ore when calcined at about 2000° F.

Extraction. From 1.0 to 2.0 pounds of nitric acid per pound of phosphorus pentoxide were used in the extraction step. The nitrogen to phosphorus pentoxide ratio in the fertilizer product was controlled by the proportion of nitric acid. Fertilizer having a nitrogen-phosphorus pentoxide weight ratio of 0.5 was produced by using about 1.0 pound of nitric acid per pound of phosphorus pentoxide; fertilizer having a weight ratio of 1.0 was produced by using about 2.0 pounds of nitric acid per pound of phosphorus pentoxide. When the latter proportions were used, over 97% of the phosphorus pentoxide was extracted. When 1.0 pound of nitric acid was used, the proportion of phosphorus pentoxide extracted varied from 90 to 97%. All of the pilot-plant tests were made with 42% nitric acid, which was available from TVA operations. The use of more concentrated acid (50 to 60%), such as is now produced in many plants, would be advantageous because a more concentrated filtrate could be produced.

Sulfuric acid was used in the extraction step to improve the filterability of the extraction slurry and to control the water solubility of the phosphorus pentoxide in the fertilizer product. The sulfuric acid reacted with the calcium in the ore to form calcium sulfate, which served as a filter aid. About 0.3 to 0.4 pound of sulfuric acid per pound of phosphorus pentoxide was sufficient for satisfactory filtration. However, about a 1 to 1 ratio was used in most tests to obtain increased water solubility of the phosphorus pentoxide.

The water solubility of the phosphorus pentoxide in the fertilizer product varied from about 5 to 30%. The data of Table I show that the water solubility of the phosphorus pentoxide in the product could be increased by decreasing the calcium-aluminum to phosphate mole ratio. This mole ratio could be controlled within limits by the proportion of nitric and sulfuric acids used in extraction. The aluminum to phosphate mole ratio was not affected significantly by the amounts of acids used. The calcium to phosphate mole ratio in the filtrate could be decreased by increasing the proportion of sulfuric acid or, to a lesser extent, by decreasing the proportion of nitric acid.

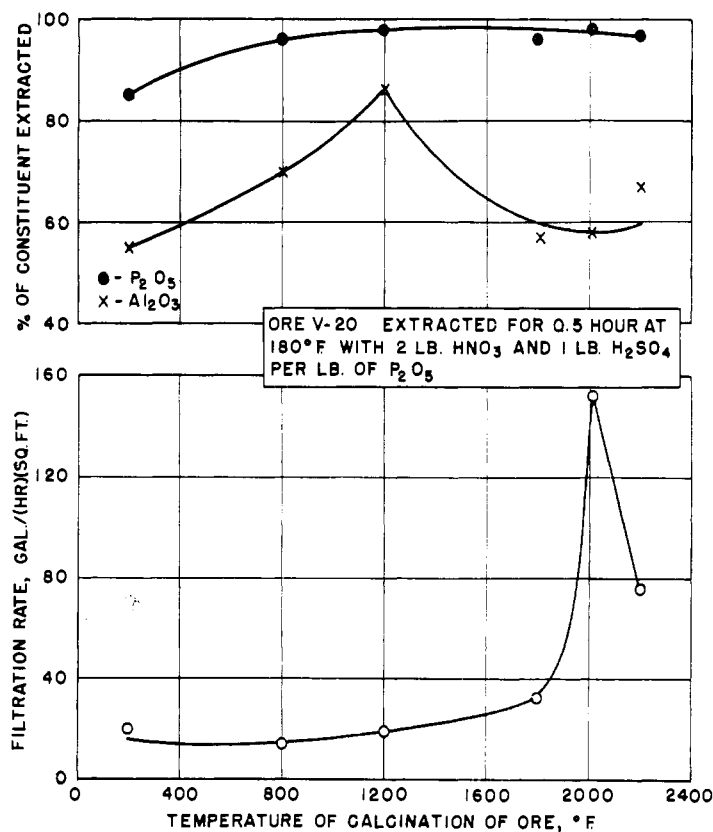


Figure 2. Effect of calcination temperature of ore on the filtration rate of the extraction slurry and the extraction of P₂O₅ and Al₂O₃

Table I. Effect of Acid Proportions on Mole Ratios and Effect of (Ca + Al):P₂O₅ Mole Ratio on Water Solubility of P₂O₅

Extraction, Weight Ratio		Fertilizer Product, Mole Ratio			Water Solubility of P ₂ O ₅ in Fertilizer Product, % of Total P ₂ O ₅
HNO ₃ :P ₂ O ₅	H ₂ SO ₄ :P ₂ O ₅	Ca:P ₂ O ₅	Al:P ₂ O ₅	(Ca + Al):P ₂ O ₅	
V-10 Ore Calcined at 2050° F.					
1.0	0	0.81	0.67	1.48	..
1.0	0.3	0.44	0.70	1.14	..
1.0	0.6	0.33	0.60	0.93	17
1.0	1.0	0.13	0.63	0.76	26
1.0	1.5	0.08	0.61	0.69	32
2.0	0	0.92	0.62	1.54	4
2.0	1.6	0.11	0.64	0.75	22
V-20 Ore Calcined at 2100° F.					
1	1	0.21	0.82	1.03	9
2	1	0.31	0.83	1.14	11
2	1.5	0.20	0.86	1.06	9

When the calcium-aluminum to phosphate mole ratio was 1 or greater, most of the phosphorus pentoxide was present as dicalcium phosphate and aluminum phosphate with little or no ammonium phosphate. Of these compounds, only ammonium phosphate is water soluble. As this mole ratio was decreased below 1, the proportion of ammonium phosphate increased. In tests with ore V-10, the lowest calcium-aluminum to phosphate mole ratio obtained was about 0.7; about 30% of the phosphorus pentoxide was in a water-soluble form. In tests with ore V-20, the lowest ratio obtained was about 0.97 and about 10 to 15% of the phosphorus pentoxide was in a water-soluble form. It was possible to lower the mole ratio further by adding to the filtrate a water-soluble phosphorus pentoxide material such as phosphoric acid or diammonium phosphate. This addition resulted in an increase in the amount of water-soluble phosphorus pentoxide in the fertilizer product.

The extraction step was carried out in three tanks in series. Each tank was 1 foot in diameter by 3.5 feet high and was equipped with a turbine agitator, which was driven with a variable-speed air motor. The calcined ore, nitric acid, and recycle wash liquor from the filter were fed into the first tank and the sulfuric acid was fed into the third tank. The ore, which had been crushed to pass a 20-mesh screen, was fed at the rate of 450 pounds per hour. The retention time in each tank was about 10 minutes. The slurry flowed by gravity through the extraction tanks; only a few inches of freeboard were required as there was no foaming. Steam coils were used in the first two tanks to increase the temperature of the slurry to about 180° to 200° F. to promote extraction of the phosphorus pentoxide; this was particularly helpful when low proportions of nitric acid were used.

The procedure used in the extraction

step had an important effect on the filtration rate of the slurry. An adverse effect occurred if the sulfuric acid was added to the first or second tank instead

	Composition, % by Weight								
	P ₂ O ₅		N	SiO ₂	Al ₂ O ₃	CaO	SO ₄	F	Sp. Gr.
Filter cake (dry basis)	0.4	0.1	0.2	72.7	4.0	4.8	8.5	0.04	...
Filtrate	9.0	...	3.6	...	4.5	2.2	0.5	0.2	1.28

of to the third tank. The degree of agitation of the slurry after the addition of sulfuric acid also affected the filtration rate. If too little agitation was used, the slurry which was thixotropic, became too thick to flow from the third tank; filter cakes from this type slurry were difficult to wash. If too violent agitation was used, the rate of filtration decreased. The proper degree of agitation usually could be judged by the physical appearance of the slurry. Diluting the sulfuric acid to 50% was also beneficial to filtration. The solids content of the slurry usually was kept at about 32% by recycle of wash liquor from the filtering step. A higher solids content decreased the filtration rate.

The extraction slurry was filtered on a continuous belt filter with a monofilament polyethylene cloth as the filter medium. The filter had a total of 5 square feet of area available for filtering and for washing of the filter cake. About 1.2 square feet were used for filtering and the remainder for washing. Best operation was obtained when the filter cake was 3/4 inch thick. This thickness of cake was obtained with a belt speed of 1.8 feet per minute at the usual feed rate of 450 pounds of ore per hour to the extraction unit. The vacuum during normal operation was about 10 inches of mercury.

The belt filter was designed for two

stages of countercurrent washing. Typical data for operation with calcined ore V-20 were as follows: About 1.0 pound of water per pound of ore was used. The dilute wash liquor, which contained about 2% of phosphorus pentoxide, was recycled to the filter. The strong wash liquor, which contained about 5% of phosphorus pentoxide, was recycled to the extraction units. The wash sections were kept flooded to minimize cracking of the cake.

The cake broke away freely from the filter cloth as the belt passed over the head pulley. After the cake was discharged, the filter cloth was cleaned by spraying with water. Blinding of the cloth did not occur. The cake contained about 35% water. About 1 to 3% of the phosphorus pentoxide input to the process was lost as soluble material in the cake. Typical analyses of the cake and filtrate obtained when V-20 ore was extracted with 2.0 pounds of nitric acid and 1.0 pound of sulfuric acid per pound of phosphorus pentoxide are shown below:

Concentration. Concentration of the filtrate was desirable to reduce the proportion of recycle required for granulation. In pilot-plant operation, the filtrate was concentrated to about 13% of phosphorus pentoxide by batch evaporation in a steam-heated open tank. As it was not convenient in the pilot plant, bench-scale tests determined the nitrogen loss that could be expected in the concentration step. In these tests the filtrate was heated to boiling at atmospheric pressure in a flask fitted with a water-cooled condenser. The vapors were condensed and collected. The nitrogen losses were calculated from the nitrogen content and volume of the condensate. These tests showed that the filtrate made with 2 pounds of nitric acid per pound of phosphorus pentoxide could be concentrated to about 13% of phosphorus pentoxide with a nitrogen loss of less than 1%; the concentrated filtrate was fluid even when cooled to room temperature. Filtrate made with 1 pound of nitric acid per pound of phosphorus pentoxide could be concentrated to about 13% phosphorus pentoxide with a nitrogen loss of less than 0.5%. This concentrated filtrate contained a considerable amount of precipitated solids and it gelled on cooling, but could be handled if the temperature were kept above 170° F. Tests in a single-pass, centrifugal, thin-film evaporator were made by an

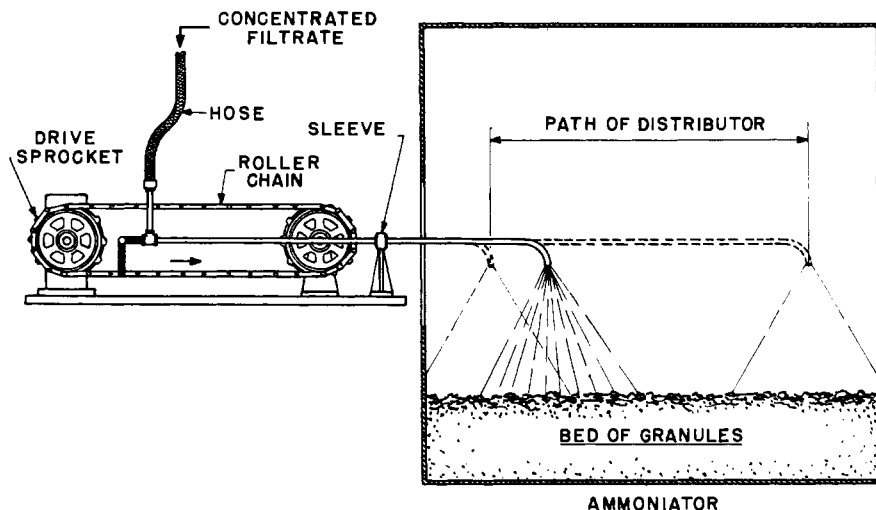


Figure 3. Filtrate distributor for continuous ammoniator

equipment manufacturer. In these tests, filtrate made with 2.0 pounds of nitric acid and 1.0 pound of sulfuric acid per pound of phosphorus pentoxide was concentrated at 15 inches of mercury (200° F.) to 13% phosphorus pentoxide with a nitrogen loss of less than 2%.

Ammoniation, Granulation, and Drying. The concentrated filtrate was processed to a fertilizer product very successfully in the TVA continuous ammoniation-granulation pilot plant (5). This type of equipment has been found to be adaptable to the ammoniation and granulation of a variety of fertilizer formulations and has been adopted widely in industry. The facilities consisted of a rotary ammoniator, a rotary granulator, a rotary dryer, a rotary cooler, and equipment for feeding and metering raw materials, screening product, crushing oversize, and recycling fines. The ammoniator, granulator, dryer, and cooler were made of mild steel.

The ammoniator, a 3- by 3-foot cylinder without flights, was operated at a speed of 15 r.p.m. and was provided with a scraper bar of 2-inch angle iron for continuous cleaning of the inside wall, and with a retaining ring for maintaining a 9-inch bed of solids.

Concentrated filtrate was distributed on the surface of the bed through an open-end pipe which was moved back and forth across the length of the bed by a mechanical device at a rate of about 28 passes per minute. A sketch of the distributor is shown in Figure 3. This type of distribution was used because the filtrate contained a small amount of solids which stopped up a conventional perforated pipe distributor. The distributor for gaseous ammonia was 30 inches long; it was of the slotted type described by Yates, Nielsson, and Hicks (9) and was positioned 7 inches below the surface of the bed. The flow of concentrated fil-

trate was metered with an orifice in a constant-head feed tank and then was pumped to the distributor. The flow of gaseous ammonia was metered through a rotameter. Product fines, which were recycled to the ammoniator for control of granulation, and potassium chloride, which was added when desired, were fed at controlled rates through volumetric feeders.

The unit was operated with concentrated filtrate (13% of phosphorus pentoxide) made by extracting V-20 ore with 2.0 pounds of nitric acid and 1.0 pound of sulfuric acid per pound of phosphorus pentoxide in the ore. The production rate for a typical run was 500 pounds of 14-14-14 (nitrogen-phosphorus pentoxide-potassium oxide) fertilizer per hour and was limited by the capacity of the dryer. At this rate and for this grade of product, it was necessary to recycle dry fines at a rate of 1.6 pounds per pound of dry product. About 22 cubic feet per minute of cooling air were blown on the material in the ammoniator, through a perforated pipe, to aid in control of granulation.

The calculated average moisture content of the materials charged to the ammoniator (including recycle) was about 17% and the moisture content of the product from the ammoniator averaged 15%. This material was in the form of hard, round granules; a screen analysis showed the size distribution to be about 6% of +6 mesh, 81% -6 +20 mesh, and 13% -20 mesh. Because of this satisfactory granulation, it probably was not necessary to use the granulator (2- by 6 $\frac{1}{2}$ -foot cylinder). However, the granulator was an integral part of the pilot plant and served the purpose of conveying the product from the ammoniator to the dryer. The temperature of the material discharged from the ammoniator was about 150° F. The mole ratio of ammonia to nitrate in this ma-

terial was 1 to 1.17. Based on the concentration of ammonia in the exhaust gas, the loss of ammonia was less than 2%.

The dryer was 3 feet in diameter by 24 feet long. Heat was supplied, concurrently, by the combustion of natural gas in a chamber adjacent to it. With a feed rate of about 1500 pounds of wet granules per hour, the retention time was about 40 minutes. With inlet gas at 357° F. and exit gas at 230° F. and a drying gas rate of 1600 cubic feet per minute (normal temperature and pressure), the granules were dried from 15% to about 4% of water. The temperature of the product was maintained below 200° F. to minimize loss of nitrogen. Under these conditions, the loss of nitrogen was less than 2% of the nitrogen charged to the dryer.

The product from the dryer was passed countercurrent to a small flow of air through a 2- by 8-foot rotary cooler and then was screened to -6 +20 mesh. The oversize was passed through crushing rolls and this material and the fines were returned to the system for use as recycle. In order to have sufficient recycle for control of granulation, some of the onsize product also was crushed and used for this purpose.

During the early part of the work, considerable time was devoted to another method for processing the filtrate. The filtrate was ammoniated continuously in a tank, potassium chloride was added, and the resulting slurry was granulated in a pugmill with recycle fines. Prior to granulation the slurry was concentrated to reduce the amount of fines required in granulation. This method of operation was satisfactory but had some disadvantages which were avoided by use of the continuous ammoniator. The ammoniated slurry became very thick on concentration and probably would be difficult to handle in a large plant. Granulation occurred in the pugmill at 10 to 12% of moisture, which required recycle ratios of 3 to 4 pounds per pound of dry product. Also, the particle size of the granules could not be controlled as well as in the continuous ammoniator. The availability of the phosphorus pentoxide in the products obtained by both methods was at least 98.5%.

Operating Data. After methods of control were developed and satisfactory operating conditions were defined, the pilot plant was operated to demonstrate the process and to obtain data for evaluation and design purposes. A summary of operating data in a demonstration run to produce a 14-14-14 nitrogen-phosphorus pentoxide-potassium oxide fertilizer from V-20 ore is shown in Table II. Operation of the extraction and the ammoniation-granulation units was not integrated. The extraction unit was operated for two or three shifts a day and storage was provided for

the filtrate. The ammoniation-granulation unit was operated one shift a day.

Product Gases and Characteristics.

The chemical compositions of 11-22-11 and 15-15-15 leached-zone fertilizers made from ore V-10 and of 14-14-14 fertilizer made from ore V-20 are shown in Table III. In a few tests with ore V-10 the potassium chloride was omitted and 20-20-0 and 14-28-0 fertilizer was made. The phosphate compounds in the products are aluminum, calcium, and ammonium phosphates. As there is little information on the agronomic effectiveness of aluminum phosphates, the products are being tested extensively. Starostka, Norland, and MacBride (8) reported results of greenhouse tests on

Table II. Summary of Operating Data

Product grade	14-14-14
Ore used	V-20
Calcination temperature of ore, ° F.	2100
Extraction	
Ore, lb./hr.	450
Nitric acid (43%), lb./hr.	211
Sulfuric acid (50%), lb./hr.	94
Recycle wash liquor (61 g. P ₂ O ₅ /l.), lb./hr.	430
Solids in slurry, % by weight	32
Slurry temperature, ° F.	180-200
Filtration	
Slurry temperature, ° F.	160-180
Wash water, lb./hr.	450
P ₂ O ₅ lost in cake, % of P ₂ O ₅ in ore	
Soluble	2.7
Insoluble	1.2
N lost in cake, % of N in HNO ₃ feed	2
Filtration rate including cake washing, lb. ore/(hr.) (sq. ft.)	90
Ammoniation, granulation, and drying	
Production rate, lb./hr.	500
Feed rate, lb./hr.	
Concentrated filtrate (13% P ₂ O ₅ , 6% N)	553
Anhydrous gaseous ammonia	46
Potassium chloride (62% K ₂ O)	105
Recycle	800
Cooling air to ammoniator, cu. ft./ton product	5000
Product temperature, ° F.	
From ammoniator	151
From dryer	191
Moisture content of product, %	
From ammoniator	15
From dryer	4
Loss of NH ₃ from ammoniator, %	1.0
Loss of NH ₃ from dryer, %	1.3
Granulation, %	
Oversize (+6 mesh)	6
Onsize (-6 +20 mesh)	81
Undersize (-20 mesh)	13

Table III. Composition of Product

Ore	Nominal Grade	Product Analysis, Wt. %									
		N		P ₂ O ₅			K ₂ O	CaO	Al ₂ O ₃	SO ₃	H ₂ O
		Total	NH ₃	Total	W.s.	Avail-ability					
V-10	15-15-15	15.1	9.0	15.2	4.8	99.3	15.2	1.6	6.3	2.9	2.4
V-20	14-14-14	14.3	7.9	15.0	2.4	99.3	14.2	3.2	8.3	1.6	3.5
V-10	11-22-11	11.6	7.1	22.5	5.2	98.7	12.1	4.9	9.8	0.8	2.8

leached-zone fertilizer made in the TVA pilot plant. Material having 20% of the phosphorus pentoxide in the water-soluble form gave crop yields comparable with those of triple superphosphate. Materials having low water solubility were less effective. DeMent and Seatz (4) reported that field tests by state experiment stations showed the products to be generally as satisfactory a source of phosphorus as concentrated superphosphate when applied to long season crops in the southeast. In some cases the leached-zone fertilizer was less satisfactory than concentrated superphosphate in promoting early growth or as a starter fertilizer for corn. The degree of water solubility was of minor importance in final yields on long season crops of the southeast. However, the leached-zone fertilizers having at least 20% of the phosphorus pentoxide in the water-soluble form were usually more effective than fertilizers of lower water solubility in increasing yields of early forage crops and as a starter fertilizer for corn. Field tests are being continued.

Bag-storage and drillability tests of pilot-plant products were made independently by the U. S. Department of Agriculture (7) and the Tennessee Valley Authority. These tests showed that the storage properties of the pilot-plant products were very good and their drilling characteristics were excellent.

Recovery of Uranium. Over 90% of the uranium in the ore went into solution in the extraction step. The uranium could be recovered from the extract by a process involving solvent extraction. A discussion of the process is beyond the scope of this paper.

Further Work. Leached-zone ore is different from the ores normally used as a source of phosphate, and the fertilizer industry will not be in a position to use it until experimental production and field demonstration of the product made from it are completed. TVA plans to construct a semicommercial-size plant for the demonstration of the process developed in the pilot plant. The successful demonstration of the process will encourage industry to use the material now wasted. This in turn will reduce the cost of mining the phosphate going into fertilizer, will extend the life of the Florida phosphate reserves, and will help

in the national defense by making possible the recovery of a significant domestic source of uranium.

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