

Table III. Analysis of Pilot Plant Products

Feed Composition, %		Product Composition, %							Available P ₂ O ₅	P ₂ O ₅ availability
Phosphate rock	Gypsum ^a	CaO	SO ₃	F	SiO ₂	R ₂ O ₃	P ₂ O ₅			
33 ^b	67 ^c	51.1	17.2	1.19	13.8	1.8	14.5	10.2	70	
30 ^b	70 ^c	51.1	20.4	0.78	15.2	1.3	13.6	12.0	88	
25 ^d	75 ^c	48.1	18.8	0.80	20.0	3.0	10.1	9.4	93	
30 ^b	70 ^e	47.7	33.0	0.97	5.2	1.0	11.6	11.0	95	

^a Anhydrous basis. ^b Phosphate rock A. ^c By-product gypsum. ^d Phosphate rock B. ^e Mineral gypsum.

during fusion and it appeared as a glassy, dark green slag. Approximately 47% of the sulfur present was lost as sulfur dioxide in the flue gas. It was not feasible to determine the sulfur dioxide content in the flue gas in this or subsequent runs.

The mixture containing 70% of by-product gypsum gave a product which was satisfactory. It had a phosphorus pentoxide availability of 88% and contained 12.0% of citric acid soluble phosphorus pentoxide. It was highly viscous, but flowed more easily and shattered to a greater degree on quenching than did the products from mixtures containing less gypsum. This product also had a glassy, green appearance after quenching.

When a mixture containing 75% of by-product gypsum and 25% of phos-

phate rock was used, the melt flowed easily from the furnace, shattered very well on quenching, and gave a granular product with a 93% phosphorus pentoxide availability. The availability based on solubility in neutral ammonium citrate varied from 80 to 90%.

Mineral gypsum, in the proportion found to be optimum in previous work, was used for control fusions (7). The product was chalky white, granular, and had a 2% citric acid-soluble phosphorus pentoxide content of 11.0%. Considerably less sulfur dioxide was lost during fusion, as evidenced by its chalky appearance, and the fact that a lower fusion temperature was required. The analysis of the product is shown along with those for the by-product gypsum fusion in Table III.

It was demonstrated on a pilot plant scale that phosphate rock can be fused

with by-product gypsum to give a product suitable as a fertilizer. The product has the advantage of nonacidity, is nonhygroscopic, and does not need to be ground after quenching. Inasmuch as wet process gypsum is an undesirable by-product, the fusion process provides a use as well as a method for its disposal.

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FERTILIZER TECHNOLOGY

High-Analysis Phosphate Fertilizers from Normal Superphosphate

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Normal superphosphate can be converted into dicalcium phosphate, monocalcium phosphate, and phosphoric acid by washing with water, and concentrating the water extract. Dicalcium and monocalcium phosphates are formed in the solid phase as concentration proceeds, and can be separated. Some of these solids have a low F/P₂O₅ ratio as is required for feed supplements. A crude acid can be obtained. Triple superphosphates with from good to excellent physical properties can be prepared by solubilizing phosphate rocks with this crude acid. Concentrated normal superphosphate water extract can also react with phosphate rock at 150° to 200° C. to produce a high-analysis phosphate fertilizer. Other process modifications are possible.

NORMAL SUPERPHOSPHATE is used primarily for direct application as such and for the preparation of fertilizer mixtures. Limited quantities have been used in South Africa as a source of low-fluorine, water-soluble feed supplement (20). More recently, Bridger, Horzella, and Lin have shown that it can react with phosphate rock to produce a dicalcium phosphate fertilizer (3). It has found few other commercial applications.

A process is proposed, by which normal superphosphate can be converted into several high-analysis phosphate ferti-

lizers. The reactions involved are well known (2-4, 8, 14, 17-20, 24-26). The process suggests a number of possibilities, some of which appear commercially feasible.

Figure 1 indicates the products which can be prepared from normal superphosphate.

Materials and Analytical Methods

Three phosphate rock samples with the analysis shown in Table I were used.

Total, water-soluble, and citrate-insoluble phosphorus pentoxide contents were determined by volumetric titration,

and the Association of Official Agricultural Chemists' (AOAC) procedures were closely followed (7). Free acid was determined by extraction with 95% alcohol according to an unofficial procedure based on the work of Hill and Beeson, and Ross (13, 22), and adopted in the control laboratories of the Taiwan Fertilizer Co. A Florida phosphate rock sample from the National Bureau of Standards was used in checking the results of phosphorus pentoxide determinations.

Calcium oxide was determined by the

Table I. Analysis of Phosphate Rocks Used

	Phosphate Rock		
	Florida	Morocco	Makatea
Chemical Analysis, ^a %			
P ₂ O ₅	33.96	33.83	37.46
CaO	48.29	51.72	51.33
Al ₂ O ₃ + Fe ₂ O ₃	2.19	0.52	0.96
CO ₂	2.72	3.88	2.45
SiO ₂	5.45	1.33	0.17
F	3.73	4.12	2.45
Screen Analysis, ^b %			
+80 mesh	8.2	0.1	16.2
-80 + 100 mesh	6.7	13.6	14.7
-100 + 150 mesh	16.9	32.6	1.2 ^c
-150 + 200 mesh	12.2	24.6	30.5
-200 mesh	56.0	29.1	37.4

^a Air-dried basis.
^b Tyler standard.
^c Reground until most passed 150-mesh.

Table II. Analysis of Normal Superphosphate^a

Constituents	%
Total P ₂ O ₅	20.07
Water-soluble P ₂ O ₅	19.55
Citrate-insoluble P ₂ O ₅	0.01
Free acid	5.20
CaO	28.36
Al ₂ O ₃ + Fe ₂ O ₃	1.03
SO ₃	30.73
F	1.66
Water solubility	97.4
Availability	100

^a Age, 1 year and 41 days; sulfuric acid used, 2.7 moles per mole P₂O₅.

usual method of permanganate titration, aluminum and iron as the mixed oxides, sulfur trioxide by weighing as barium sulfate, and fluorine by the method of Willard and Winter (10).

Preparation of Normal Superphosphate. The special feature of the proposed process calls for the preparation of a normal superphosphate with maximum water solubility. The literature contains numerous accounts as to how it might be obtained.

Of all factors, acid ratio and curing conditions are considered to be among the most influential on the conversion of phosphate rock into the water-soluble forms.

Tests were run with 100- and 300-gram portions of 72% c.p. sulfuric acid at 60° C. and acid ratios varying from 2.6 to 3.0 moles of sulfuric acid per mole of Florida rock phosphorus pentoxide. The mixtures were kept at 75° to 100° C. for 2 hours, and then cured under varied conditions of temperature and humidity.

Results showed 97% conversion of rock phosphorus pentoxide into water-soluble phosphorus pentoxide at 2.7

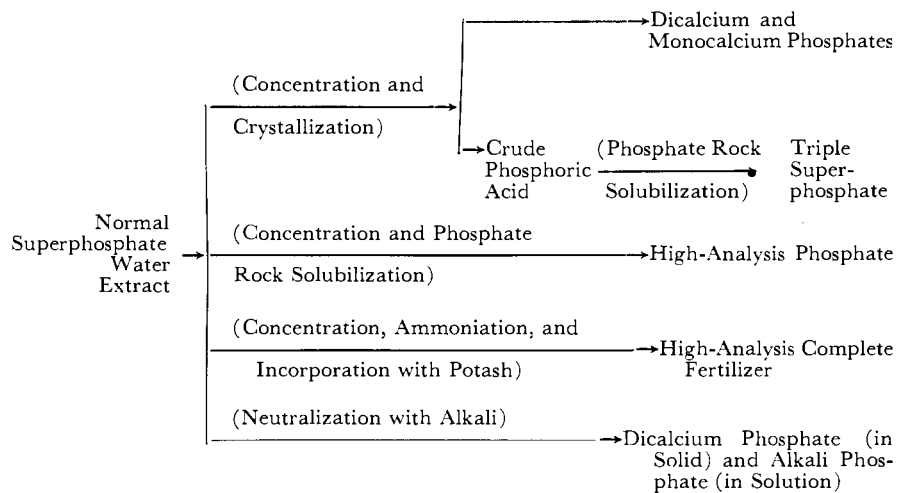


Figure 1. Preparation of high-analysis phosphates from normal superphosphate

Table III. Effect of Water-Superphosphate Ratio on Recovery of Essential Constituents in Extracts^a

Water-Superphosphate Ratio ^b	Per Cent Recovery								Mole Ratio in Extract	
	Total P ₂ O ₅	Water-soluble P ₂ O ₅	Free acid	CaO	Al ₂ O ₃ + Fe ₂ O ₃	SO ₃	F	CaO/P ₂ O ₅	F/P ₂ O ₅ ^c	
1	35.4	38.5	29.1	0	
2	44.4	46.7	62.9	2.5	41.7	0	25.3	0.20	0.351	
4	61.2	64.3	..	8.2	57.3	0.48	..	
8	70.2	73.2	79.2	13.0	61.2	0	26.5	0.66	0.232	
16	94.8	97.4	..	26.3	66.0	3.2	..	0.99	..	
32	97.1	98.9	97.3	32.1	56.3	8.9	24.1	1.18	0.157	

^a For normal superphosphate analysis see Table II.
^b Ml. water at 20° C. per gram of normal superphosphate.
^c Mole ratio $\times 0.1338$ = weight ratio.

moles of sulfuric acid per mole of phosphorus pentoxide, when thoroughly cured in open containers at room temperature. Raising the acid ratio above 2.7 did not improve the conversion, while shortening the curing time to 5 or 2 weeks reduced the water solubility to 94 or 92%. This acid ratio is higher than the current practice in many countries, but it is close to some, notably the British, where superphosphates are guaranteed to be water-soluble (15, 18).

Several normal superphosphate stock samples were prepared for use in further experiments. The composition of one typical sample is given in Table II.

Extraction of Water-Soluble Phosphate. Effect of Water-Superphosphate Ratio. The AOAC official method of analysis of water-soluble phosphorus pentoxide calls for the leaching of 1-gram sample with water to obtain a filtrate of 250 ml. (7). This water-superphosphate ratio was considered high for the proposed process to become practicable, because much heat energy would be required to concentrate the extract.

Reynolds, Pinckney, and Hill used water-superphosphate ratios of 10 to 100 in preparing low-fluorine extracts from normal superphosphate (20). Preliminary tests with the normal superphosphate sample (Table II) showed 98% removal of water-soluble phos-

phorus pentoxide for a water-superphosphate ratio of 100, and 94% for a ratio of 25.

Ten-gram portions of the normal superphosphate sample were placed on 15-cm. rapid-filtering papers and washed under gravity with 10, 20, 40, 80, 160, and 320 ml. of water at 20° C. The wet residues were thoroughly drained and dried at 105° C. for 3 to 6 hours or longer, weighed, and analyzed for total and water-soluble phosphorus pentoxide, free acid, calcium oxide, aluminum, and iron mixed oxides, sulfur trioxide, and fluorine. Recoveries of these essential constituents in the water extracts were obtained by difference, and are shown in Table III.

The data are plotted as shown in Figure 2. Recoveries of total phosphorus pentoxide, water-soluble phosphorus pentoxide, free acid, and calcium oxide were directly proportional to the logarithm of the water-superphosphate ratio, but that of fluorine remained almost constant within the range of ratios tested. The recovery of aluminum and iron mixed oxides increased rapidly at first, but soon slowed down. Sulfur trioxide was the last to appear in the extract. These curves give some idea as to how the presence of aluminum and iron oxides and sulfur trioxide in the extracts could not be limited significantly except

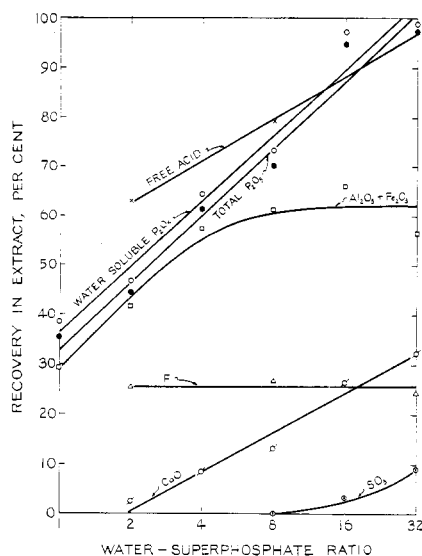


Figure 2. Recovery of essential constituents in extracts vs. log of water-superphosphate ratio

with drastic loss of phosphorus pentoxide.

Effect of Method of Extraction. The recovery of water-soluble phosphorus pentoxide and of total fluorine was somewhat different from the data of Reynolds, Pinckney, and Hill. This was due, among other factors, to the difference in the method of extraction (20).

Ross and Adams found that washing normal superphosphate under gravity gave higher results of water-soluble phosphorus pentoxide than washing under suction (27). Agitation, alone or followed by prolonged standing, might give different results. The temperature of the water used appears to be another important factor.

Tests were run with the sample by direct washing, agitation followed by immediate filtration, and agitation plus prolonged standing with water at 15°, 55°, and 90° C. The residues were dried and analyzed, and per cent recoveries computed by difference.

The results are tabulated in Table IV. Direct washing under gravity was the most effective means of extracting all the essential constituents. The recoveries by direct washing were somewhat independent of temperature except for aluminum and iron oxides, and for sulfur trioxide, where higher temperature seemed to favor the formation of a less soluble sulfate. Agitation lowered the recovery of all constituents. The higher the temperature, the lower was the recovery. With agitation, lower recovery of total phosphorus pentoxide was accompanied by a very slight reduction in recovery of water-soluble phosphorus pentoxide. This was due to the conversion of monocalcium and dicalcium phosphates into more basic and insoluble forms (especially in the presence of fluorine) with simultaneous liberation of phosphoric acid (3, 8, 18, 27).

Table IV. Effect of Extraction Conditions on Recovery of Essential Constituents from Normal Superphosphate^a

Extraction Method	Water Temp., ° C.	Recovery, %					CaO/P ₂ O ₅ Mole Ratio in Extract
		Total P ₂ O ₅	Water-soluble, P ₂ O ₅	CaO	Al ₂ O ₃ + Fe ₂ O ₃	SO ₃	
Washing ^b	15	96.0	98.4	29.1	59.2	10.9	1.09
	55	96.7	99.0	29.4	63.1	9.4	1.09
	90	96.4	98.8	27.7	68.0	8.3	1.03
Agitation ^c	15	94.9	98.3	25.9	27.1	5.0	0.98
	55	93.4	97.2	25.4	18.4	4.1	0.97
	90	89.6	97.1	23.0	24.3	3.7	0.92
Agitation ^d	15	94.2	97.7	26.8	44.7	8.7	1.02
	55	93.5	97.6	27.9	41.7	8.0	1.07
	90	91.1	96.9	24.9	35.9	5.3	0.98

^a 10.0 grams normal superphosphate (see Table II) extracted with approximately 260 ml. of water. ^b Under gravity. ^c 30-minute hand stirring followed immediately by filtration. ^d Same as ^c, except that mixture was allowed to stand for 48 hours, then warmed up again to temperature indicated.

The above data point to the fact that washing under gravity is the most suitable means for maximum recovery of water-soluble phosphorus pentoxide, and that controlling the water-superphosphate ratio or water temperature might not significantly reduce the contamination of some constituents such as aluminum and iron oxides and sulfur trioxide.

Dicalcium Phosphate-Monocalcium Phosphate Crystallization. Monocalcium phosphate tends to decompose in water solutions into dicalcium phosphate and phosphoric acid. The conversion, according to the data of Bassett, Elmore and Farr, and Campbell and Coutts, varies as the monocalcium phosphate concentration and also as the temperature. For the same temperature, the conversion increases with concentration until a maximum is reached, and then drops abruptly (4, 8, 18, 19).

Table IV shows that the average calcium oxide/phosphorus pentoxide mole ratio in normal superphosphate water extracts was only slightly higher than that required for monocalcium phosphate. Thus, the extracts contained substantially dissolved monocalcium phosphate. To find out how such an extract would behave during concentration, 2 kg. of a 1-year-old normal superphosphate (a plant scale product) was washed, under gravity, with water until the filtrate measured 9500 ml. After a few days' standing, the first lot of solid phase was removed, and the solution was concentrated at 100° C. to about half its original volume, and then cooled down to room temperature (12° to 17° C.). Alternate solid removal and solution concentration were repeated several times, applying essentially the technique of "fractional precipitation" in the manufacture of low-fluorine dicalcium phosphate from wet-process acid (5, 6).

The solids and solutions were analyzed for phosphorus pentoxide, calcium oxide, sulfur trioxide, and fluorine. Results in Table V show that the first four lots of

solids removed had a phosphorus pentoxide availability of 97.2 to 99.6%, and a phosphorus pentoxide water solubility of 7.6 to 33.1%, indicating that they were mostly dicalcium phosphate. The fifth lot of solid contained substantially monocalcium phosphate, as can be judged from the water solubility and the average calcium oxide/phosphorus pentoxide mole ratio of 0.99. The fluorine/phosphorus pentoxide weight ratio decreased rapidly to 0.003, which is comparable to or lower than for some defluorinated or low-fluorine phosphates produced for feed purposes (5-7, 12, 25, 27).

The solubility of calcium sulfate varies as the phosphorus pentoxide content of the solution, and shows a maximum within an optimum phosphorus pentoxide concentration range. It changes with the temperature of the solution, and is different for different hydrates (14, 17). Campbell and Coutts showed that in the system calcium oxide-phosphorus pentoxide-sulfur trioxide-water at 75.3° C., gypsum was the stable form up to 30% phosphorus pentoxide (4). These facts and other published information (18, 19, 26) indicate that concentration of normal superphosphate water extract will within a certain phosphorus pentoxide concentration range precipitate gypsum in large quantities. Such changes were observed in the second and third concentrates, and were reflected in the low total phosphorus pentoxide contents and the high calcium oxide/phosphorus pentoxide mole ratios of the solids removed.

Physical properties of most of the solids removed were good, except for the fifth lot, the drillability of which was poor. This was due to the incomplete separation of phosphoric acid.

The change of phosphorus pentoxide in solution was gradual, as could be expected from the data of Bassett and others (4, 8, 18, 19).

The above observation indicates that stepwise removal of the solids has the advantage over crystallization as a single

Table V. Effect of Concentration on Composition of Normal Superphosphate Water Extract

	Concentrate No.									
	1 ^a		2		3		4		5	
	Solid phase ^b	Liquid phase	Solid phase ^b	Liquid phase	Solid phase ^b	Liquid phase	Solid phase ^b	Liquid phase	Solid phase ^b	Liquid phase
Total P ₂ O ₅ , %	34.02	3.19 ^c	26.66	5.81 ^c	28.51	10.88 ^c	45.73	18.42 ^c	53.32	27.75 ^c
P ₂ O ₅ water solubility, %	7.6	..	33.1	..	13.7	..	12.3	..	88.0	..
P ₂ O ₅ availability, %	99.6	..	97.2	..	99.6	..	97.7	..	100	..
CaO, %	..	1.03 ^c	30.71	1.89 ^c	33.84	3.48 ^c	37.40	4.65 ^c	20.53	5.33 ^c
SO ₃ , %	0.54	0.65 ^c	16.81	0.58 ^c	17.36	0.63 ^c	5.04	0.69 ^c	1.79	0.27 ^c
CaSO ₄ , ^d %	0.92	..	28.58	..	29.51	..	8.65	..	3.04	..
CaO/P ₂ O ₅ mole ratio	2.92	..	3.01	..	2.07	..	0.99	..
F/P ₂ O ₅ weight ratio	0.228	..	0.146	..	0.039	..	0.025	..	0.003	..
Weight recovered, grams	3	..	35	..	14	..	79	..	128	..
Volume, liters	..	9.5	..	4.2	..	1.9	..	0.9	..	0.2

^a Prior to any concentration. ^b Removed before further concentration. Washed with acetone, and dried at 105° C. ^c Expressed as grams per 100 grams solution. ^d Computed from SO₃ content.

product in the possibility of tailoring to meet specific purposes, such as high water solubility and low fluorine content.

Triple Superphosphate Preparation.

As the conversion of monocalcium phosphate into dicalcium phosphate and phosphoric acid decreases rapidly while the solution phase is being saturated with respect to monocalcium phosphate (8), it appears very difficult to obtain from normal superphosphate water extract by concentration alone phosphoric acid free from dissolved monocalcium phosphate. The crude acid so obtained as shown in Table V contained 27.75% phosphorus pentoxide, 5.33% calcium oxide, and 0.27% sulfur trioxide. Neglecting the effect of sulfur trioxide on calcium oxide requirement, the acid contained 14.26 grams of surplus acid phosphorus pentoxide per 100 grams of acid more than required for forming monocalcium phosphate with the calcium oxide present.

To show how this acid might react with phosphate rock, crude acid-rock mixtures with acid ratios of 2.1 and 2.3 moles of surplus acid phosphorus pentoxide per mole of rock phosphorus pentoxide were prepared. These ratios are lower than the current practice of slightly above 2.3 (2, 19, 26). The mixtures were heated with stirring to a sirupy consistency, and cured for 1 month in open containers in the laboratory. The Meyers process was followed.

The products had from good to excellent physical properties. The phosphorus pentoxide water solubilities ranged from 91.9 to 94.6%, and the availabilities from 96.3 to 98.2%. Thus, the crude acid from normal superphosphate had satisfactorily served its purpose (Table VI).

Treatment of Phosphate Rock with Normal Superphosphate Water Extract. The above discussions indicate that normal superphosphate water extract, after concentration at 100° C. to a sirupy consistency, will contain dicalcium phosphate, monocalcium phosphate, phosphoric acid, calcium sulfate (mostly gypsum), and a little apatite. This

Table VI. Triple Superphosphate from Crude Phosphoric Acid^a and Phosphate Rock

Phosphate Rock Treated ^b	Acidulation Ratio ^c	P ₂ O ₅ in Product, ^d %			P ₂ O ₅ Water Solubility, %	P ₂ O ₅ Availability, %
		Total	Water-soluble	Citrate-insoluble		
Florida	2.1	48.84	44.90	1.83	91.9	96.3
	2.3	49.20	46.26	1.26	94.0	97.4
Morocco	2.1	49.26	45.24	1.23	91.8	97.5
	2.3	49.74	46.80	0.90	94.1	98.2
Makatea	2.1	50.78	47.64	1.54	93.8	97.0
	2.3	50.60	47.84	1.15	94.6	97.7

^a Liquid phase of No. 5 concentrate (see Table V). ^b See Table I. ^c Moles surplus acid P₂O₅ per mole rock P₂O₅. ^d Age, 1 month.

might be used as a substitute for monocalcium phosphate for solubilizing phosphate rock according to the method of Bridger, Horzella, and Lin (3).

Preliminary tests using straight normal superphosphate showed considerable difficulties, particularly at the conversion step. Tests with normal superphosphate water extracts introduced new factors, which required precise control. At the suggestion of Sauchelli and Bridger (23), the conversion step was first standardized with pure monocalcium phosphate. Subsequently, conversion was then applied to rock-normal superphosphate mixtures. Tests with rock-normal superphosphate water extracts came last.

Since then, numerous tests have been made and the procedure finally adopted was as follows. Normal superphosphate was thoroughly cured until maximum phosphorus pentoxide water solubility was reached. A 20-gram portion was washed, under gravity, with water until the filtrate measured 1 liter. The water extract (or normal superphosphate-water or pure monocalcium phosphate-water mixture) was concentrated, and the calculated amount of phosphate rock was added, when the concentrate measured about 100 ml. The mixture was heated to dryness at 110° C. The cake was wet-ground with 3 to 4 times its

weight of water and then transferred to a 250-ml. beaker. Four cycles of conversion were then applied; each cycle consisted of 3 hours heating at 185 to 200° C., wet-grinding, and heating to a sirupy consistency. The products were ground to pass 80-mesh, or 60-mesh, when too much gummy material was present, and analyzed for phosphorus pentoxide water solubility and availability. Fineness of grinding had little effect on solubility determinations.

The procedure was more elaborate than that of Bridger, Horzella, and Lin (3), but compared with the latter, refluxing had been omitted. The use of an electric oven in place of an oil bath had made it possible to run simultaneously as many as 12 samples. Results as shown in Table VII compare favorably with most of those of Bridger, Horzella, and Lin (3). Table VIII shows that high-analysis products with high availability could be obtained by treating Florida, Morocco, and Makatea rocks with normal superphosphate water extracts.

During the preparation of the products for analysis, the presence of a gummy material was noted. Bridger, Horzella, and Lin found that there was evidence of amorphous material in their conversion products (3). It was suspected that some pyro- and metaphosphates might have been formed (9, 24, 25). Qualita-

tive tests with albumin, silver nitrate, and zinc sulfate (10) confirmed the presence of pyrophosphate in many samples, and indicated that there was evidence of the presence of metaphosphate. It appears therefore that a more suitable name for the conversion products would be high-analysis phosphate fertilizer, as was suggested by Hignett and Hoffmeister (17).

Other Process Modifications. There appear to be some other ways, by which normal superphosphate can be converted into high-analysis products. Its water extract can be neutralized with ammonia or sodium carbonate (or sodium hydroxide), precipitating dicalcium phosphate and leaving behind in solution ammonium or sodium phosphate (25). The water extract can also be concentrated, mixed with potash, and ammoniated to produce a high-analysis complete fertilizer.

Reduction of the fluorine content might raise the value of the dicalcium phosphate from normal superphosphate as a feed supplement. This might be done by treating the water extract first with sodium chloride (5, 6), and then with small amounts of calcium carbonate or lime to remove the dissolved fluorine as apatite (16, 20).

Some of these tests are in progress in this laboratory.

Acknowledgment

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Table VII. Standardization of the Monocalcium to the Dicalcium Phosphate Conversion Procedure^a

Test No.	Acid Ratio	Pre-liminary Curing, ^b Days	Conversion Conditions			Total P ₂ O ₅ , %	P ₂ O ₅ Availability, %
			Temp., ° C.	Treatment time, hours	No. of cycles		
Tests with Pure Monocalcium Phosphate ^c							
S-1 ^d	1.0 ^e	7	150-160	3	3	50.22	92.8
S-16	1.0 ^e	7	150-200	3	6 ^f	50.14	96.5
Tests with Straight Normal Superphosphate ^h							
S-30	2.1 ^f	7	150-200 ^g	3	6 ^g	24.00	86.7
S-32	2.3 ^f	7	150-200 ^g	3	6 ^g	23.24	92.3
Tests with Normal Superphosphate Water Extract ^h							
S-51	2.1 ^f	..	185-200	3	4	42.67	93.8
S-53	2.3 ^f	..	185-200	3	4	43.40	97.3

^a Florida phosphate rock used throughout all tests.
^b After heating to sirupy consistency.
^c Made by May and Baker Ltd., Dagenham, England.
^d Wet grinding omitted for this test.
^e Mole acid P₂O₅ from monocalcium phosphate per mole rock P₂O₅ (3).
^f Moles SO₃ in normal superphosphate (based on analysis) per mole P₂O₅ in normal superphosphate and rock.
^g 3 cycles at 150°-160° C. plus 3 cycles at 185°-200° C.
^h See Table II.

Table VIII. Reaction of Different Phosphate Rocks with Normal Superphosphate Water Extract^a

Test No.	Phosphate Rock Used ^b	Acid Ratio ^c	Grams Super ^d	Grams Rock	P ₂ O ₅ in Product, %			P ₂ O ₅ Availability, %
					Total	Water-soluble	Citrate-insoluble	
S-51	Florida	2.1	5.71	42.67	10.61	2.67	93.8	
S-52	Florida	2.2	7.14	42.50	13.73	2.77	93.5	
S-53	Florida	2.3	9.09	43.40	11.73	1.18	97.3	
S-54	Morocco	2.1	5.71	42.47	10.72	2.84	93.3	
S-55	Morocco	2.2	7.14	43.37	15.28	2.34	94.6	
S-56	Morocco	2.3	9.09	42.94	16.87	0.32	99.3	
S-57	Makatea	2.1	6.25	43.66	10.24	3.02	93.1	
S-58	Makatea	2.2	8.00	43.27	13.34	1.34	96.9	
S-59	Makatea	2.3	10.00	43.47	15.69	0.68	98.4	

^a See Table II.
^b See Table I.
^c Moles SO₃ in normal superphosphate per mole P₂O₅ in normal superphosphate and in rock.

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