A METHOD
FOR THE
MANUFACTURE OF PHOSPHATE FERTILIZER

Thesis

by

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A SULFITE PROCESS FOR THE MANUFACTURE OF PHOSPHATE FERTILIZER.

Among the foods that must be supplied to plants by fertilization of the soil one of the most important is phosphate. Manure and commercial fertilizers supply phosphate to some degree, but the standard method for introducing phosphates into the soil in quantity is by the use of superphosphate. This product is made by treating phosphate rock, which consists chiefly of the insoluble calcium phosphate, $Ca_3(PO_4)_2$, with concentrated sulfuric acid. Superphosphate is a mixture of $CaHPO_4$, $Ca(H_2PO_4)_2$, $CaSO_4$, some free phosphoric acid and some unconverted calcium phosphate. In addition to these substances superphosphate always contains all of the impurities that were present in the original rock and acid.

The chief advantage of superphosphate is its low cost of production. The large producers of superphosphate are often smelters of sulfide ores and get their sulfuric acid as a by-product of the smelting industry. Phosphate beds also frequently lie close to the smelting plants so that transportation of the raw

materials to the superphosphate works is no great problem. Manufacturing costs are low, for the process consists essentially of grinding the rock, mixing it with sulfuric acid, allowing it to stand in a brick lined pit until it stops reacting and cools, then pulverizing it and sacking it for market.

The disadvantages of the superphosphate are (1) that it is subject to reversion and (2) that it contains a lot of inactive material that runs up the freight bill.

These disadvantages are done away with by a "double superphosphate" method used in Europe. A quantity of phosphate rock is decomposed with enough dilute sulfuric acid to set free all of the phosphate as H_3PO_4 and to precipitate all of the calcium as $CaSO_4$. The material is filtered and the phosphoric acid solution is concentrated by evaporating in lead pans. Ground phosphate rock in the proper quantity to form monocalcium phosphate is added to the phosphoric acid. The fertilizer obtained in this way contains no gypsum or other sulfate and is more concentrated that superphosphate.

A step further toward concentration is the introduction of a cation with fertilizing value in place of the calcium in combination with the phosphate. This has been done by the American Cyandmide Company in their

product "Ammo-Phos", which contains twenty percent of ammonium and twenty percent of phosphate.

The object of the present research is to investigate the possibility of duplicating "Ammo-Phos" or of making a product of a similar nature according to the idea of Mr. Henry Blumenberg, as covered by several U. S. patents held by him.

Mr. Blumenberg's idea was to treat a mixture of a solution of ammonium sulfate, calcium nitrate and ground phosphate rock with sulfur dioxide and an excess of air, precipitating the calcium as $CaSO_4$ and obtaining a solution of ammonium phosphate. After filtering, the remaining SO_2 was to be driven off by heating, the solution cooled and neutralized with ammonia to separate out iron, aluminum and any remaining calcium, then evaporated until the ammonium phosphate crystallized out on cooling.

METHODS OF TESTING

The solid matter in the treaters was tested at intervals for phosphate content. When any treater was discharged a test for citric acid soluble phosphate also was made, as citric acid soluble phosphate is classed commercially as soluble. The difference between the two values thus obtained is the net insoluble phosphate

spoken of below.

Samples of 500 cc were drawn from the treaters and filtered by suction. The precipitate was dried on porous plates upon a sand bath until all the water had been removed, then it was powdered and allowed to cool in a desiccator. 5.000 grams were weighed out and placed in a Kjeldahl flask with a small quantity of a 50-50 mixture of concentrated nitric and sulfuric acids. The flask was carefully heated so that the charge did not regurgitate, with the addition of more of the mixed acid if necessary, until the solid matter in the bottom of the flask was white, indicating that the digestion was complete. The contents of the flask were cooled and diluted to 250 cc in a volumetric flask. 10 cc of this diluted solution were pipetted into a clean beaker, and diluted to about 100 cc. 20 cc each of concentrated nitric acid and ammonia were added and the solution was heated to 70°C. 10-40 cc of ammonium molybdate solution were added, according to the amount of phosphate believed to be present, and the solution was allowed to stand on the water bath for about half an hour at 60°. The precipitate was filtered at and washed with a hot 1% solution of KNO_3 until it was free of acid. The precipitate was removed to a beaker and a 0.2 normal

solution of NaOH was run in until the precipitate had dissolved. The excess of NaOH was titrated back with 0.2 normal HCl.

For the citric acid soluble test, 5.000 grams of the powdered solid were placed in a beaker and about 300 cc of a 2% citric acid solution were added. The whole was heated at 60° for an hour, then filtered and diluted to 500 cc in a volumetric flask. 50 cc were pipetted out and treated as above to determine the phosphate content.

The HCl used was 0.2082 normal and the NaOH 0.2015. By standardizing against Na_2HPO_4, it was found that 1 cc of the base was equivalent to 0.306% of phosphate by the first test.

APPARATUS

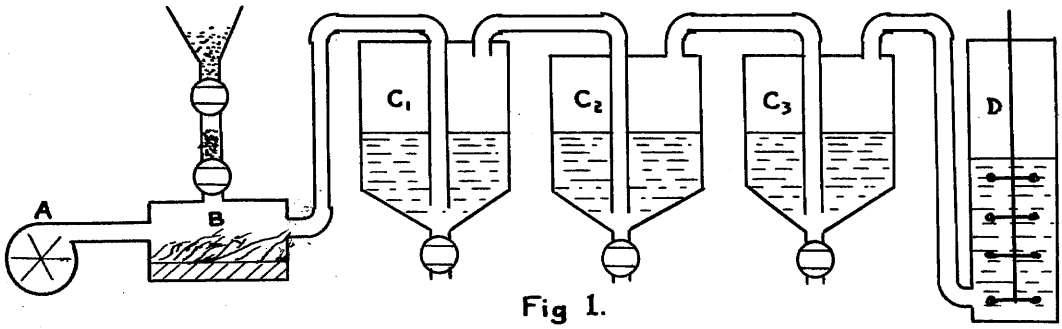


Fig 1.

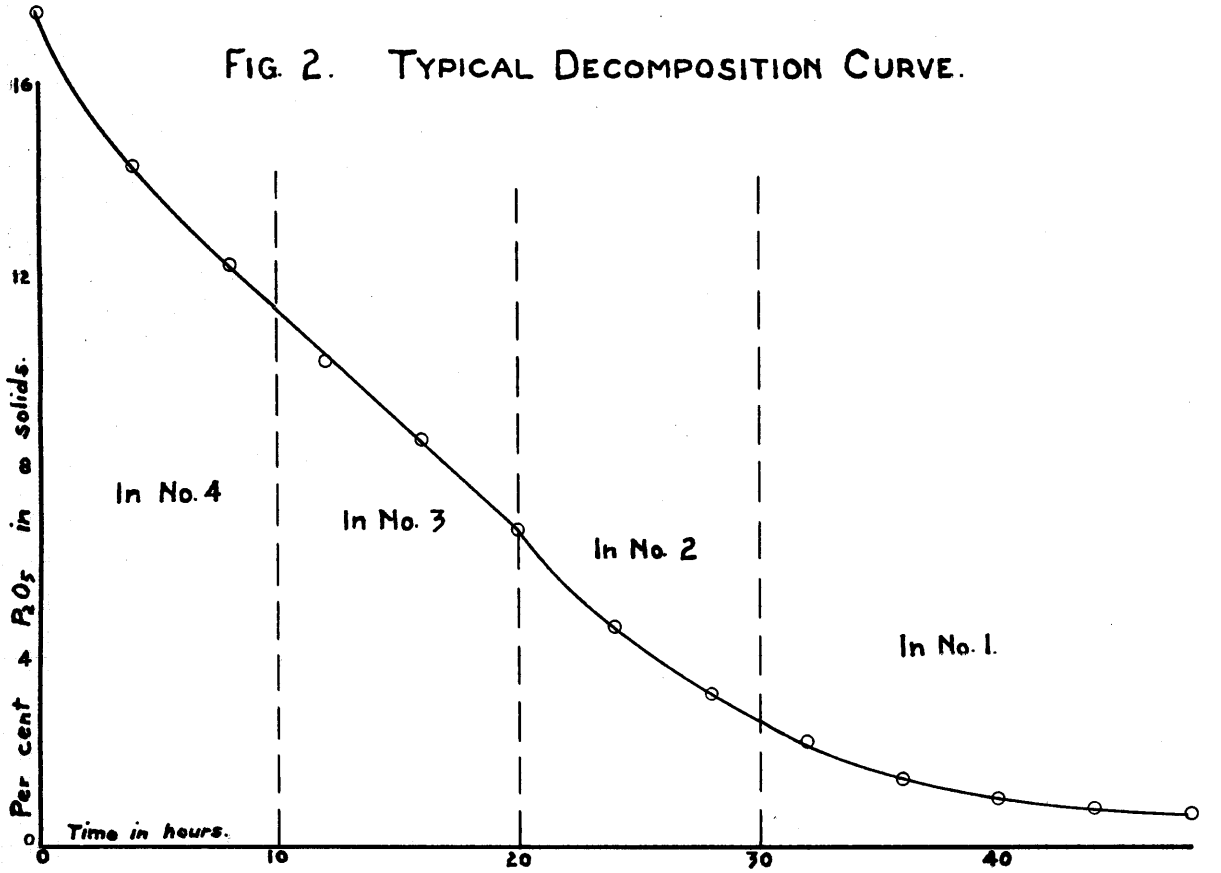
The decomposition apparatus used (see fig. 1) was designed by Mr. Blumenberg. It consisted of three lead-lined cylindrical iron chambers with conical bottoms (C) and one wooden chamber (D) equipped with

a stirring device. The lead-lined chambers had a diameter of 20 inches and a height of 24. The wooden one was 14 by 48. The sulfur burner (B) used to generate SO_2 was a cast iron chamber lined with a refractory material and designed to be fed from the top with roll sulfur through a double valve mechanism. Air was pumped through the apparatus by a Nash Hytor pump (A) of size $\frac{1}{2}$C driven by a 2 hp Century single phase motor, which also operated the stirring mechanism of the #4 treater.

DECOMPOSITION

Air compressed by the pump was sent through the sulfur burner, where part of it was converted to SO_2, then into the first treater. The gases were sent down a lead pipe nearly to the bottom of the cone, then allowed to bubble up through the liquor and out through a pipe leading to the second, third and fourth treaters in series. The waste gases were allowed to escape after passing the fourth treater. In each chamber was a charge consisting originally of ten gallons of water and six pounds each of ore, ammonium sulfate and calcium nitrate. This charge was recommended by Mr. Blumenberg as the one that had given the best results in his preliminary work. The treatment was carried on until the amount of net

FIG. 2. TYPICAL DECOMPOSITION CURVE.



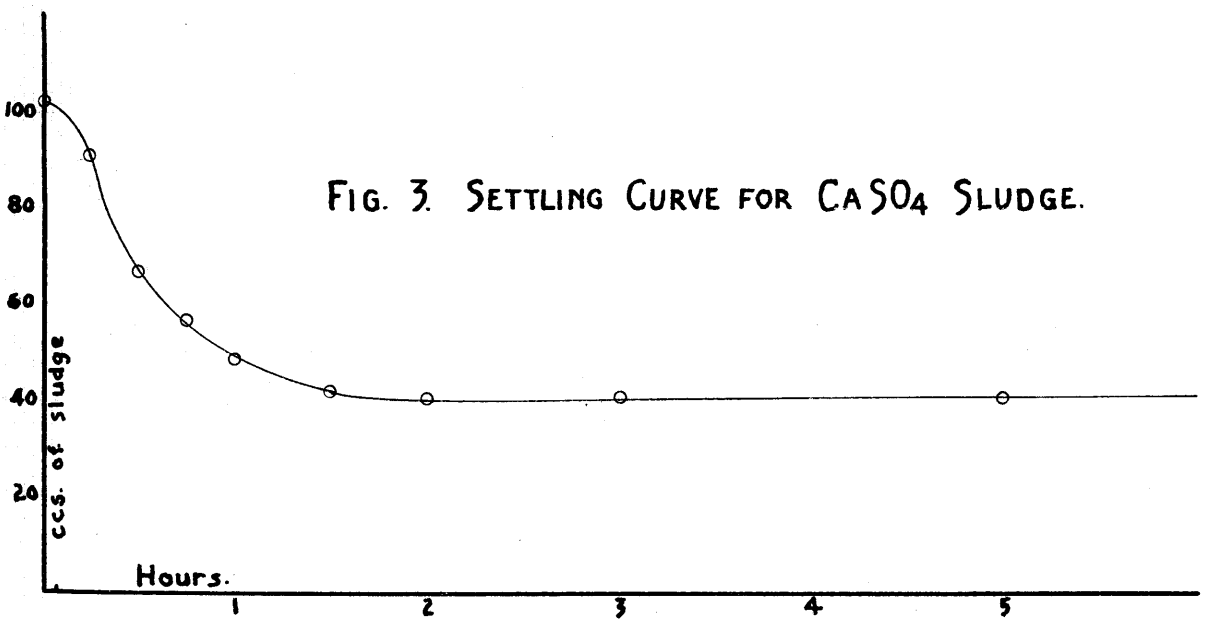


FIG. 3. SETTLING CURVE FOR $CaSO_4$ SLUDGE.

insoluble phosphate in the charge was brought down to 1% of the total insoluble matter. This was found to require about forty hours (see fig. 2). In order to secure uniform treatment and obtain maximum absorption efficiency for the apparatus used, each new charge was started in #4 treater and moved forward one step every ten hours. Sulfur was burned at the rate of one pound per hour, hence the sulfur consumption amounted to ten pounds per charge.

The following table shows more clearly what goes into the charge:

From;	(pound equivalents)			
Ore (28% P_2O_5)	Ca. 0.071	SO_4	NH_4	PO_4 0.071
Ammonium sulfate		0.091	0.091	
Calcium nitrate	0.053			

Although the actual reactions involved in the process were not investigated in this work, they may be postulated to be as follows:

1. The ammonium sulphate and calcium nitrate, both being soluble, react metathetically and precipitate calcium sulphate:

$$(NH_4)_2 SO_4 + Ca(NO_3)_2 = 2\ NH_4 NO_3 + CaSO_4$$

As is evident from the above table, there is an excess of

ammonium sulphate above the amount necessary to complete this reaction.

2. The sulfur dioxide, dissolving in the water to form sulfurous acid, attacks the phosphate rock and brings it into solution: $Ca_3(PO_4)_2 + 6H_2SO_3 = 3Ca(HSO_3)_2 + 2H_3PO_4$

3. The excess of ammonium sulfate precipitates the calcium thus dissolved: $Ca(HSO_3)_2 + (NH_4)_2SO_4 = 2NH_4HSO_3 + CaSO_4$

There is, however, not enough sulfate added to react with all of the calcium of the ore in addition to the calcium of the $Ca(NO_3)_2$, so that part of the calcium must remain in solution as long as the solution is kept saturated with SO_2. If the calcium nitrate were not added, enough sulphate would be present in the charge to more than take care of the calcium from the ore; and since the nitrate ion apparently plays no part in the process and is not recovered in the final product, it would seem that the calcium nitrate might well be omitted from the charge. Mr. Blumenberg states, however, that previous work indicated that when it is omitted, the rate of decomposition is materially lowered. Experiments to check this point should be worth while.

The solution obtained from the digestion, there-

fore, may be considered to be a mixture of ammonium, calcium, nitrate, phosphate, sulfite and sulfate ions, together with aluminum and iron, and a trace of vanadium, coming from the impurities of the ore. From this solution it is desired to obtain monammonium phosphate.

At this point it might be pointed out that, if oxidation of the SO_2 to sulfate be disregarded, all of the calcium of the phosphate rock is precipitated by sulfate coming from sulfuric acid (since the ammonium sulphate is prepared from sulfuric acid), and the only function of the SO_2 is to acidify the solution. Therefore the alleged economy of the process, apart from all other considerations, is to be questioned on this one score alone.

FILTRATION

The next step after decomposition is the filtration of the solid material. It was thought that the filtration could be made easier by allowing the solids to settle and decanting the supernatant liquid. As an experiment, a trough was constructed 3 inches high, 4 inches wide and 24 inches long, with cross-pieces half an inch high placed every 4 inches along the bottom. The suspension from the treaters was made to flow along this trough, but with the slowest stream obtainable no appreciable settling took place. To determine more accurately the rate

of settling, four 100 cc cylinders were filled with the sludge and allowed to stand for several hours. Readings were taken of the top of the sludge layer at intervals to prepare the accompanying plot (fig.3).

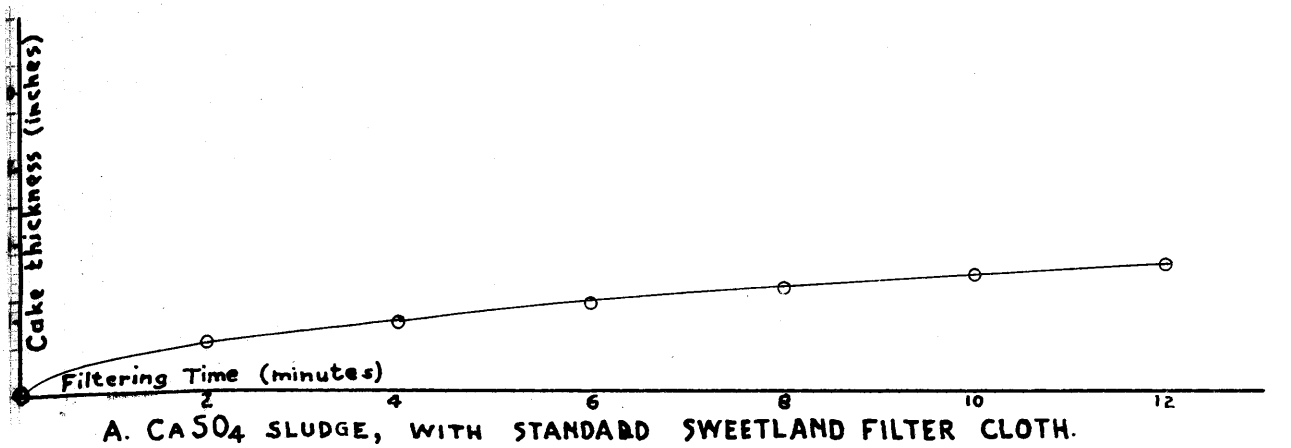
In the actual filtering work an eight inch Sweetland filter leaf operating on a vacuum of 15 inches of mercury was used. Five runs were made using different cloths and treatments:

(1) Standard Sweetland filter cloth.
(2) Six ounce canvas, close weave.
(3) Same as (2), seams waxed.
(4) Same as (1), seams waxed, precoated with filter-cel.
(5) Same as (4), but no filter-cel.

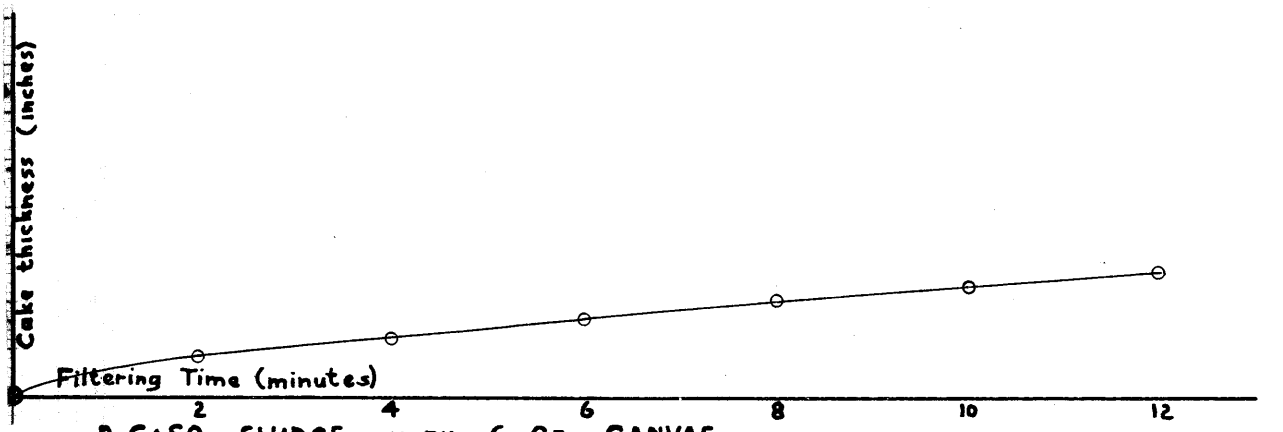
The rate of cake formation was found to vary only with the cloth used; that is, (1), (4), and (5) agreed on one rate, and (2) and (3) agreed on another very similar rate. Runs (1) and (2) gave muddy filtrates, (3), (4), and (5) gave clear ones. For (5), however, on continued operation the filtrate became muddy after about five gallons had been filtered. The same would probably hold true for (3) but the change would not come so quickly. (4) is then the only really satisfactory procedure.

REMOVAL OF SO_2.

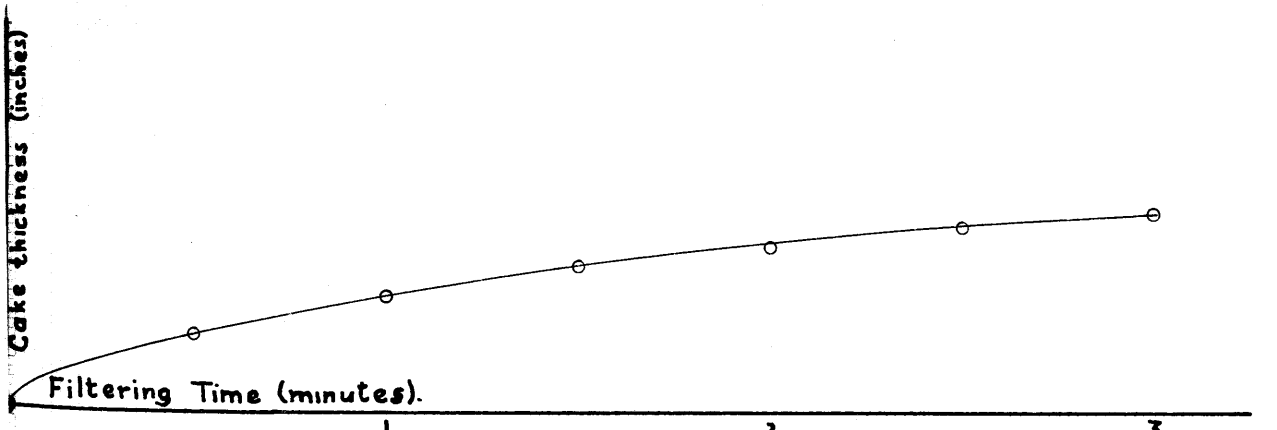
During the vacuum filtration, as might be expected, the solution lost SO_2, resulting in an acidity



A. $CaSO_4$ SLUDGE, WITH STANDARD SWEETLAND FILTER CLOTH.



B. $CaSO_4$ SLUDGE, WITH 6-OZ. CANVAS.



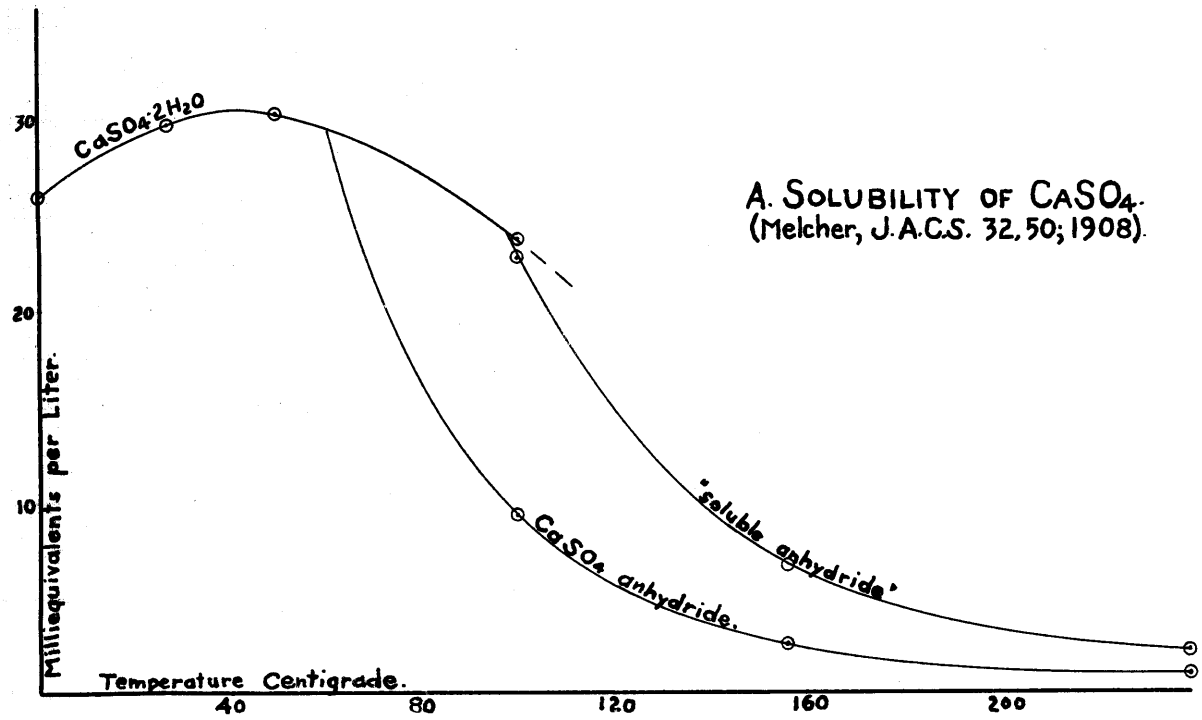
C. NEUTRALIZED SLUDGE, WITH 6-OZ. CANVAS.

FIG. 4. FILTRATION CURVES.

decrease from 0.219 N. to 0.178 N. It was thought that this acidity might be cut down much further by heating, and a test run was made to determine the point. Ten gallons of filtered solution were heated in an enamel lined steam-jacketed kettle. As no power was available to operate the mechanical stirrer, the top of the kettle was removed to permit operation as an open kettle.

When the temperature of the liquid reached about 60°, there began to form a white precipitate which did not redissolve upon cooling. This was undoubtedly calcium sulfate, which is present at saturation for the hydrated form (gypsum) in the original solution, and which partially precipitates as the much less soluble anhydrous form at that temperature (see fig. 5d). This phenomenon was exhibited whenever the solution was heated or evaporated; and since the anhydrite does not readily revert to the more soluble hydrate, but remains as an insoluble precipitate even after remaining for a month in contact with solution at room temperature, it proved to be a serious factor in subsequent evaporation and crystallization.

The heating was extended over a period of two hours. Samples of liquid were taken at fifteen-


A. Solubility of $CaSO_4$.
(Melcher, J.A.C.S. 32, 50; 1908).
$CaSO_4 \cdot 2H_2O$
"soluble anhydride"
$CaSO_4$ anhydride.
Milliequivalents per Liter.
Temperature Centigrade.
30
20
10
40
80
120
160
200

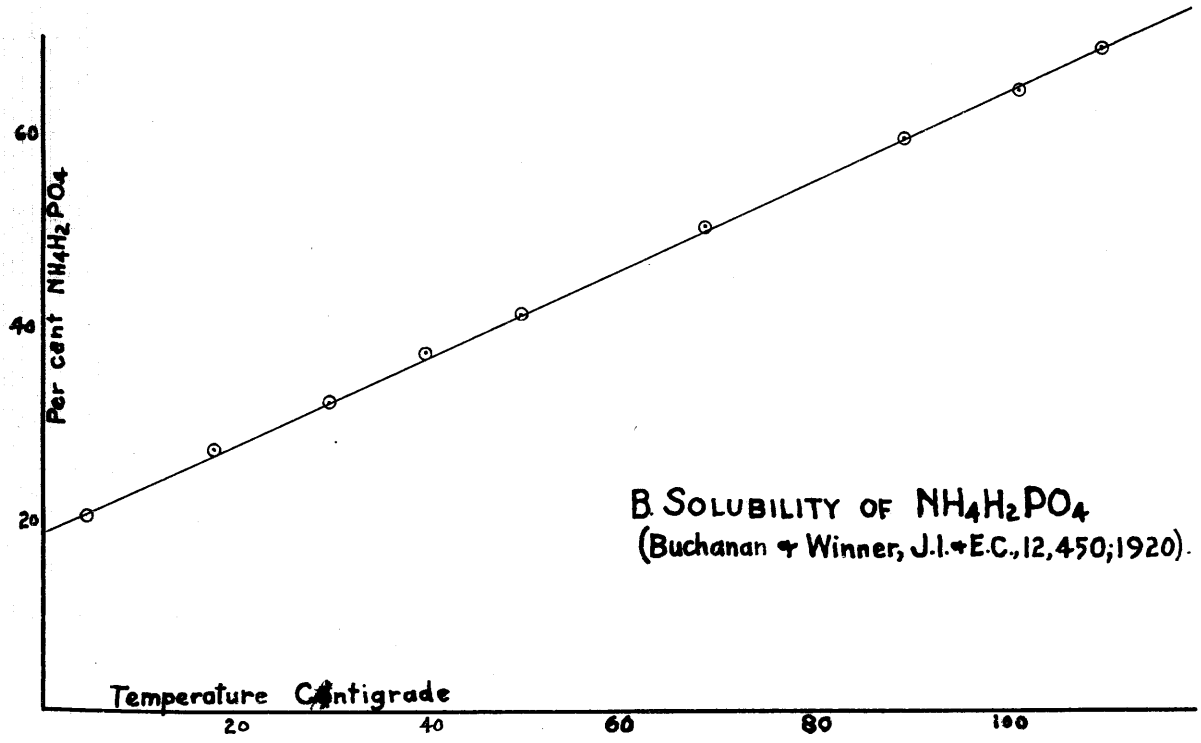

B. Solubility of $NH_4H_2PO_4$
(Buchanan & Winner, J.I.&E.C., 12, 450; 1920).
Per cent $NH_4H_2PO_4$
Temperature Centigrade
60
40
20
20
40
60
80
100

FIG. 5.

minute intervals and titrated for acidity against NaOH, using methyl orange, with the following results:

Table 1.

Time. (hours)	Temp. (°C)	Vol. of sol. (liters)	Acidity (normality)	Total equivalents of acid present
Before filtration	22	37,9	0.219	8.30
After filtration	22	37.9	.178	6.74
0.25	69	37.9	.162	6.13
0.50	91	37.9	.162	6.13
0.75	98	36.4	.170	6.17
1.00	98	34.8	.172	5.98
1.25	98	32.9	.178	5.87
1.50	98	31.4	.185	5.83
1.75	98	29.9	.191	5.72
2.00	98	28.0	.203	5.68

It can be seen that it is impossible to reduce the amount of acid appreciably below a certain amount by this treatment. The acidity of the solution is due therefore not to SO_2 but rather to nonvolatile acids, probably sulfuric or phosphoric. It is obviously inefficient to heat, cool, then reheat the solution

to evaporate it. Likewise it is useless to attempt to neutralize the solution with ammonia while it is hot. The economical thing to do is to eliminate either the first heating or the neutralization.

The solubility of monammonium phosphate was investigated (See fig. 5b.). On account of the steepness of the slope it is possible to obtain crystals by boiling down to saturation at the boiling point and then allowing the solution to cool.

Samples of the partially concentrated liquor obtained above were taken. One was neutralized with concentrated ammonia, the other was not. These two samples were boiled down to a volume, 30 cc, approaching saturation in $NH_4 H_2 PO_4$, filtered hot and allowed to crystallize. The results of this experiment are shown in the following table:

	A	B
Vol. sample	300 cc	300 cc
Vol. ammonia	------	11 cc
Evap. to	30 cc	30 cc
wt. crystals	13.1335g	3.596g
wt. for analysis	.5035	.5000
cc standard base	4.33	12.85
% P_2O_5	13.2	39.3
Purity, basis of $NH_4H_2PO_4$	21.4%	63.6%

When the ammonia was added a rather heavy aluminum - iron precipitate came down. As is seen from the above table it is necessary to remove this in order to obtain crystals containing much phosphate. Consequent-

ly it seems best to eliminate the first heating, and to neutralize the filtrate from the first filtration. The neutralized solution is also easier to filter when hot because there is not so much precipitated matter to remove and the solution seems less viscous.

This leaves the process in a state where a filtration is made, a reagent is added to the filtrate and then another filtration is made immediately. If the sludge from the treater could be neutralized before filtering one operation of the filtering apparatus could be avoided. The liquor filtered would be neutral or alkaline instead of acid, so that less expensive filtering apparatus could be used. The one disadvantage of this procedure would be that more ammonia would have to be used to take care of the SO_2 that otherwise would be taken off by the vacuum pump of any suction filter that should be used in the unneutralized sludge. This is not such a disadvantage, however, because the depreciation of the suction apparatus would be much less in the absence of this corrosive gas.

Ten gallons of sludge out of the treaters were neutralized with 2.3 liters of concentrated ammonia and filtered with the No. 4 filter setup. The filtrate was

clear, but it was obvious that the filtration cycle must be short, for the rate of flow through the cake decreased very rapidly with the time.

CRYSTALLIZATION

Time was not available to investigate crystallization on a larger scale. The only crystallization work done was that in connection with the neutralization problem above.

YIELD

The filtered, unneutralized liquor tested 4.39% P_2O_5. From the solubility curve of monammonium phosphate it can be calculated that the maximum yield in one crop of crystals is about 1.2 pounds of monammonium phosphate from each batch treated. The initial substances going into the process are:

phosphate rock	6 lb.
ammonium phosphate	6 lb.
calcium nitrate	6 lb.
sulfur	10 lb.
ammonium hydroxide, conc.	5 lb.

To the cost of these materials must be added the operation, depreciation and interest in an expensive plant, consisting of at least four treaters, a sulfur burner, filter presses, evaporation system, crystal driers, etc. Even assuming that the calcium

nitrate is omitted, that the sulfur consumption is reduced to a tenth of its present amount and that the ammonia is recoverable (necessitating an ammonia recovery plant), the process does not seem practicable. Labor in such a plant would have to be skilled to a greater extent than in most fertilizer plants, as most of the apparatus is specialized and requires an intimate knowledge for its efficient operation.

CONCLUSIONS:

The method suggested by Mr. Blumenberg can be improved by:

(a) The use of more efficient treaters, which will reduce sulfur consumption.

(b) The omission of calcium nitrate from the original charge.

(c) Neutralization of the charge before filtering, omitting the heating to remove sulfur dioxide.

Even with these improvements, it seems inevitable that the process cannot hope to compete with other methods of treating phosphate rock.

SUMMARY:

A new method for the treatment of phosphate rock has been investigated in its most important

phases (digestion, neutralization, filtration and yield). The major difficulties in each of these steps have been considered with the result that certain changes in the process have been recommended.

Further work on the problem, if undertaken, should include studies of the problems of evaporation and crystallization, as well as the feasibility of recovering the small amount of vanadium present in the ore.

The investigators acknowledge the cordial cooperation of The Stockholders' Syndicate of Los Angeles, who instigated the research and provided the apparatus, and of Dr. W. N. Lacey of California Institute of Technology, under whose direction the work was performed.