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Utilization of unwashed low grade phosphate rock.

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UTILIZATION OF UNWASHED LOW GRADE PHOSPHATE ROCK

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UTILIZATION OF UNWASHED LOW GRADE PHOSPHATE ROCK

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A B S T R A C T

A method for the production of phosphoric acid from low grade, unwashed phosphate rock by leaching with sulfuric acid was developed. Determinations were made of the effects upon the acid-rock reaction of impurities in the rock, temperature of reaction, concentration of acids, amount of acid for complete reaction, and pre-treatment of rock. A phosphoric acid of 25 per cent strength was obtained.

Methods are described for the production of sodium phosphate by fusing or leaching phosphate rock with sodium carbonate, sodium hydroxide, sodium chloride, and sodium sulfate.

Defluorination of phosphate rock is performed by treating phosphate rock with sulfur at elevated temperatures. A defluorinated phosphate rock containing less than one per cent fluorine is then obtained.

INTRODUCTION

Phosphate rock is classified as high, medium, or low grade, depending on its phosphorus content. High grade phosphate rock contains at least 32 per cent P_2O_5 (phosphorus pentoxide) and is used for the production of high grade phosphate fertilizers [1], and phosphoric acid by the wet process [2,3]. Medium grade rook contains 20 to 30 per cent P_2O_5 and is used for the production of phosphoric acid and phosphate chemicals by the electric [4] and blast-furnace processes [5], as well as for the production of phosphate fertilizers. Phosphate rock containing less than 20 per cent P_2O_5 is classified as low grade rock, and as yet has not been put to any commercial use.

It is usually necessary to beneficiate or up-grade the raw rock by either flotation or water washing to obtain the phosphorous content necessary for commercial use. The phosphate rook found in Florida and the Western states can be beneficiated by flotation. This is not the case with the Tennessee phosphate rock. For the most part Tennessee rook can only be up-graded by water washing.

From a technical standpoint, one of the most important and one of the most difficult of the problems facing the phosphate industry is the recovery or elimination of the large quantities of phosphates which are now lost during the mining and preparation of Tennessee phosphate rock for commercial use. These losses result, essentially, from the inability to mechanically separate the phosphate particles from the undesirable

impurities such as silicon, iron, and aluminum compounds (6).

Of equal importance is the utilization of low grade phosphate rock to replenish the decreasing deposits of phosphate rock of a high quality. This depletion of high quality phosphate rock is particularly noticeable in the Tennessee deposits.

The phosphate reserves of the United States are 13,286,700,000 long tons (7), or 51 per cent of the world's total. The rock mined in the United States in recent years, as shown in Table I (8) shows large increases in tonnage mined during the past few years.

TABLE I. PHOSPHATE ROCK MINED IN THE UNITED STATES (LONG TONS)

Year	Florida	Tennessee	Western States	Total
1934	2,464,969	394,311	38,958	2,898,238
1941	3,417,900	1,301,067	201,876	4,920,843
1943	3,274,266	1,868,407	227,294	5,369,967
1945	3,814,935	1,260,849	323,955	5,399,739

This rate of mining does not seem cause for alarm when the reserves are considered, but mining of Tennessee phosphate rock is decreasing. This decrease is a result of the depletion of high quality rock.

For most treatments of Tennessee phosphate rock, it is usually necessary to up-grade the mined rock by washing, to obtain the phosphorus content required. This washing operation,

while increasing the per cent phosphorus, results in the loss of 50 per cent of the phosphorus found in the original rock. The phosphorus carried off with the wash water is in the form of a colloidal suspension, and as such also presents a serious disposal problem.

It is the purpose of this work to utilize low grade, unwashed phosphate rock for the production of phosphoric acid and phosphate chemicals. The work also includes the treatment of phosphate rock to yield a product suitable for a cattle food.

The bulk of phosphate rock is used for the production of phosphate fertilizer. Being a material involving large quantities of low unit value, fertilizer has its economic feasibility dependent upon raw material costs. With low grade phosphate rock, it is not economically practical to manufacture a fertilizer to compete with a fertilizer made from higher grade rock; consequently, low grade rock must be used for manufacture of products other than fertilizers. Greater margin is provided between selling price and manufacturing costs in the phosphate chemical field. This field offers a possible means of utilizing poor grades of phosphate rock.

HISTORICAL

Phosphorus was first isolated by a German alchemist,
Brandt (9), in 1669, by distillation of urine. It was given
the name "phosphorus mirabilis", (Miraculous bearer of light)
by the early alchemists (10). Gahn (11) discovered the exist-
ence of calcium phosphate in bones, but it was not until 1771,
when Scheele published this information, that phosphorus was
obtained from bone-ash.

Phosphoric acid was produced by Readman and co-
workers in 1888 by an electric process (11), which was the
forerunner of the present day electric furnace process.
Readman, in 1890, also prepared phosphoric acid by treating
bone-ash with sulfuric acid.

Until 1920, all of the phosphoric acid produced
commercially was by the wet (sulfuric acid) method (12). The
electric furnace process for phosphoric acid production was a
result of extensive experimental work carried on by the U. S.
Bureau of Soils (13,14), and was developed on a commercial
scale by the Federal Phosphorus Company (6) in 1920 and 1921.
Work carried on by the U. S. Bureau of Soils was also instru-
mental in the development of the blast furnace method of phos-
phoric acid production (15). The first commercial blast furnace
was built by the Victor Chemical Works in 1928.

The wet method of phosphoric acid production was
renovated in 1936 by the introduction of the "Dorr-Strong Acid
Process" (16). Recent developments by the Tennessee Valley
Authority (5) on the blast furnace process has enabled this

process to compete with the electric furnace process so that currently there are three methods - wet, blast furnace, and electric furnace, employed for the production of phosphoric acid.

In the wet method (17) for producing phosphoric acid, phosphate rock containing 30-36 per cent P_2O_5, and relatively small amounts of iron, aluminum, and silica is used. The rock is ground wet with weak phosphoric acid, and 60-65° Be' sulfuric acid is added as make-up acid for full acidulation at higher acid strengths. The sulfuric acid concentration in the mix is 30-35° Be'. Finely ground limestone is added to precipitate the iron and aluminum impurities as the phosphates. The precipitated impurities and the unreacted rock are removed by means of an Oliver filter. The filtered phosphoric acid is then passed to evaporators where the acid is concentrated to 45-50 per cent phosphoric acid. The weak phosphoric acid which results from washing the filter cake is used to mix with the phosphate rock being ground and passes through the complete cycle again. This results in building up the concentration of phosphoric acid obtained from the sulfuric acid-phosphate rock reaction.

The principle employed in the electric furnace process for the production of phosphoric acid is reduction of the phosphate rock followed by the volatilization of elemental phosphorus, oxidation of the phosphorus, and subsequent hydration to form phosphoric acid (5). The phosphate rock used in the

process contains between 24 and 32 per cent P_2O_5. The rock is sintered or nodulized to facilitate the escape of phosphorus vapors (17). The sintered, or nodulized, rock is charged into the furnace with coke and silica sand. As the charge descends in the furnace shaft it is fused and the reduced phosphorus vaporized, carbon monoxide also being liberated. Air is passed in with the gases and the phosphorus oxidized to P_2O_5. The P_2O_5 is hydrated to produce an 85 per cent phosphoric acid.

An alternative method used with this process is to cool the gases coming out of the furnace and collect the condensed phosphorus under water. This permits the carbon monoxide to be recovered and used as a fuel gas. The condensed phosphorus can be sold as such or oxidized to P_2O_5 and hydrated to phosphoric acid. A by-product of the electric furnace is ferrophosphorus which is drawn off with the slag. The slag itself can be used as aggregate for road construction or in concrete.

As in the electric furnace process, the blast furnace process is based on the volatilization of elemental phosphorus. This process uses phosphate rock containing 22 to 32 per cent P_2O_5; the process actually favoring the rock having the lower P_2O_5 content (5). In this process the rock is pulverized and mixed with ground coke. This mixture is compressed into briquettes (17). The briquettes are dumped into the top of the furnace along with silica. Hot air is passed into the furnace and "blast furnace gas" containing elemental phosphorus and carbon monoxide is liberated. This gas is passed through

cyclone separators to remove any dust material that might be entrained. The blast furnace gas is then ignited to form CO_2 and P_2O_5 and the heat of combustion is used in the hot blast stoves to produce hot blast air. The P_2O_5 is converted directly to 85 per cent phosphoric acid. A valuable by-product from this process is ferrophosphorus which passes out with the slag.

Recent work done by the Tennessee Valley Authority on the blast furnace process has eliminated the briquetting of the phosphate rock and coke. The Tennessee Valley Authority has also developed a method of preferentially oxidizing the blast furnace gas (phosphorus and carbon monoxide) so that all of the phosphorus is converted to P_2O_5 and practically none of the carbon monoxide is oxidized. This allows the carbon monoxide to be used as a fuel gas. It is expected that this development will rejuvenate the blast furnace process.

Typical analyses of the phosphate rocks used in the wet (3), electric furnace (18), and blast furnace processes (5) are shown in Table II.

Table III (7) gives the raw material, power, and labor requirements of the three different methods of phosphoric acid production. It should be noted that these requirements are based on a resultant phosphoric acid strength of 46.5 per cent for the wet process, 85 per cent for the electric furnace, and 100 per cent for the blast furnace. From these tables it can be seen that the two furnace processes not only use a lower quality rock than the wet process but also yield a highly pure product. A factor in favor of the wet process is the small

cyclone separators to remove any dust material that might be entrained. The blast furnace gas is then ignited to form CO_2 and P_2O_5 and the heat of combustion is used in the hot blast stoves to produce hot blast air. The P_2O_5 is converted directly to 85 per cent phosphoric acid. A valuable by-product from this process is ferrophosphorus which passes out with the slag.

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TABLE II. ANALYSIS OF PHOSPHATE ROCK USED IN H_3PO_4 PRODUCTION

Components	Wet Process (%)(3)	Electric Furnace Process (%)(18)	Blast Furnace Process (%)(5)
P_2O_5	32.00	31.3	25.60
CaO	44.20	45.4	36.70
Fe_2O_3	0.53	1.8	3.60
Al_2O_3	1.25	1.8	8.30
SiO_2	5.60	10.2	18.00
F_2	1.10	3.3	2.35
Volatiles	7.20	2.6	1.00
Others	8.12	-	-

TABLE III. RAW MATERIALS, POWER, AND LABOR REQUIREMENTS FOR
H_3PO_4 PRODUCTION PER TON OF 100% H_3PO_4

	Wet Process	Electric Furnace Process	Blast Furnace Process
Strength of Acid (%)	46.5	85	100
Phosphate Rock (lbs.)	5,050(a)	4,670(a)	6,000(b)
Sulfuric Acid (lbs.)	4,190	-	-
Water (gals.)	16,130(c)	-	75,000
Steam (lbs.)	1,678	-	-
Electricity (kw-hr.)	112.9	4,060	4(d)
Direct Labor (man hrs.)	1.7	0.6-1.12	2-4
Silica Rock (lbs.)	-	1,493	1,500
Coke (lbs.)	-	880	7,000
Air (cu. ft.)	-	-	450,000

(a) 32% P_2O_5

(b) 27% P_2O_5

(c) Chiefly for cooling

(d) For Cottrell precipitators only

initial cost of the equipment and cheapness of raw materials. Also, only small power or fuel requirements are needed. The economic feasibility of the electric furnace process depends on a cheap source of electricity. This is not the case with the blast furnace method but it requires relatively large amounts of coke and water.

Of the phosphate chemicals produced for chemical use, trisodium phosphate is the most important (19). The industrial importance of trisodium phosphate is due in part to its properties of hydrolyzing in a water solution to give a high pH solution well buffered against neutralization and its ability to easily form soft and granular precipitates with heavy metal ions, such as magnesium, iron, aluminum, and calcium. Because of these properties, trisodium phosphate has been used extensively as a water softener (17).

Intensive research during the past decade on the alkali metal salts of the various phosphoric acids has resulted in the development of new and commercially useful sodium phosphate salts (20). Of the sodium phosphates recently developed, sodium metaphosphate, sodium tripolyphosphate, sodium pyrophosphate, and sodium orthophosphate are of the most importance industrially. The Hall Laboratories (21) have been instrumental in the adaptation of these salts for water conditioners.

Many grazing ranges in the United States are so depleted of available phosphorus that cattle grazing on these ranges have a phosphorus deficiency. As a supplemental source

of phosphorus, defluorinated phosphate rock has been found very satisfactory (22). Because of the toxicity of fluorine, it is necessary that its presence in phosphatic materials used as cattle food be less than four-tenths of one per cent.

Fox and his associates (23) removed 80 to 99 per cent of the fluorine present in superphosphate by heating for a comparatively short period of time at 600°C or above. The resultant tricalcium phosphate compared favorably with bone meal as mineral supplement for cattle feed.

Elmore (24) claims total removal of fluorine from phosphate rock by fusing at temperatures of 1600°C. Phosphate rock has been 95 per cent defluorinated by workers at T.V.A. (25) by heating the rock until molten, usually to 1450-1600°C. No mention is found anywhere in the literature of defluorination of phosphate rock at temperatures below 1000°C.

The prominent role played by the Tennessee Valley Authority in the development of the phosphoric acid and phosphate industry warrants special mention in a review of the history of this industry. References to work done by the T.V.A. appear throughout this section. The T.V.A. has performed, and is performing, a great number of experiments at the pilot plant level which have, and will, help the phosphate industry as a whole (26-30).

These briefly-mentioned developments and processes of the phosphate industry do not, of course, include all of the activities of the industry. They do serve, however, to show the current trend of the phosphate industry.

THEORETICAL

Tennessee phosphate rock occurs for the most part in Silurian and Devonian strata. Most of the rock is found in the Silurian strata and in the transition strata between the two. The brown rock lies in strata formation with layers of clay and earth overburden (31). Phosphate rock is an apatite ore "which may be of organic origin but the more extensive bedded deposits probably represent chemical precipitates of marine origin and variable purity. Residual deposits have been formed by phosphatic limestone being leached of their lime carbonate" (32).

The reaction of apatite with sulfuric acid, depending on the amount of sulfuric acid used, can yield monocalcium phosphate, dicalcium phosphate, and phosphoric acid, together with calcium sulfate and unreacted calcium fluoride. The reactions can be written as follows:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 3H_2SO_4 = 6CaHPO_4 + 3CaSO_4 + CaF_2$$

$$6CaHPO_4 + 3H_2SO_4 = 3Ca(H_2PO_4)_2 + 3CaSO_4$$

$$Ca(H_2PO_4)_2 + H_2SO_4 = 2H_3PO_4 + 3CaSO_4$$

$$CaF_2 + H_2SO_4 = H_2F_2 + CaSO_4$$
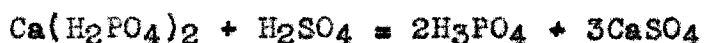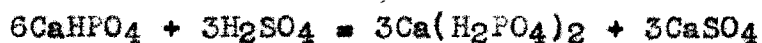
With an excess amount of sulfuric acid, all phosphates will convert in time to phosphoric acid so that the reaction of apatite with excess sulfuric acid can be written approximately as:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$
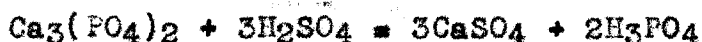
With less than the required amount of sulfuric acid, a mixture of $CaHPO_4$, $Ca(H_2PO_4)_2$, and H_3PO_4 is possible.

In a phosphate-bearing rock there are other constituents, described as impurities, besides apatite which will react

with the sulfuric acid or otherwise affect the reaction. Fore-most among these impurities are iron, aluminum, silicon, and calcium (as the carbonate). Iron and aluminum compounds may react with sulfuric acid to produce soluble sulfates. Silicon, as silica, for the most part does not react with sulfuric acid. Calcium carbonate forms insoluble calcium sulfate when acted upon by sulfuric acid.

From the foregoing, it can be seen that the phosphoric acid produced by the wet process must be treated to remove iron and aluminum impurities before a final product can be obtained. A slight reduction in the acidity of the phosphoric acid favors the precipitation of ferrous iron and aluminum as the phos-phates. The removal of ferrous iron and of aluminum results in the loss of two-thirds of an atomic weight of phosphorus, or two atomic weights, depending on the precipitate form, for every atomic weight of ferrous iron and one atomic weight of phosphorus for every atomic weight of aluminum present as impurities. Ferric iron forms soluble complexes in the presence of excess phosphoric acid, and cannot be removed in this manner. Effectively, for every atomic weight of ferric iron present in solution one atomic weight of phosphorus is tied up. The above is shown in the following simplified equations:

$$3FeSO_4 + 2H_3PO_4 = Fe_3(PO_4)_2 + 3H_2SO_4$$

$$FeSO_4 + 2H_3PO_4 = Fe(H_2PO_4)_2 + H_2SO_4$$

$$Al_2(SO_4)_3 + 2H_3PO_4 = 2AlPO_4 + 3H_2SO_4$$

$$Fe_2(SO_4)_3 + 2H_3PO_4 = 2FePO_4 + 3H_2SO_4$$
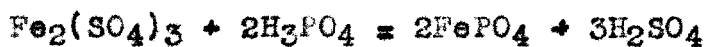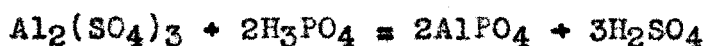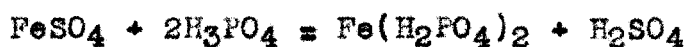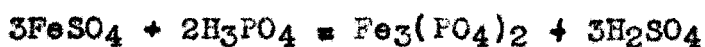
The above reactions take place as the pH of the solution is raised. The iron phosphate has been observed to precipitate at a pH as low as 2. The aluminum phosphate begins to precipitate at a slightly higher pH.

There is reason to believe that calcination of phosphate rock tends to suppress to a certain extent the formation of a soluble iron or aluminum phosphate, without affecting the conversion of calcium phosphate to phosphoric acid. Such calcination would result in the formation of iron and aluminum compounds relatively inert when acted upon by sulfuric acid.

The stoichiometric or theoretical amount of sulfuric acid for acidulation is a fictitious value, based on the amount of sulfuric acid required to react with the calcium, iron, and aluminum oxides in the rock. This value, however, is very useful as a basis on which to report results. The need for such a basis can readily be seen when it is realized that the phosphate in the rock is present not only as calcium phosphate but also as the iron and aluminum phosphates.

Phosphate rock can be defluorinated by heating until a molten stage is reached (1450°C.). Phosphate rock containing high percentages of iron and aluminum oxide (10%) along with silica can be defluorinated most easily, as these materials act as fluxing agents (25). Maximum defluorination is obtained at a silica-lime ratio of 0.38. As the silica-lime ratio increases above 0.38, the thickness of the crust on the melt increases, decreasing efficiency of defluorination. A furnace atmosphere

of nitrogen and water vapor only is essential for good defluori-
nation. At a temperature of 1500°C the per cent of water vapor
in the furnace atmospheres between 2 and 40 per cent has very
little effect on defluorination. At a temperature of 1600°C
this is not the case. The per cent fluorine removed increases
as per cent water vapor in atmosphere increases.

Working with 5 to 40 gram charges of phosphate rock,
heated in platinum-rhodium boats in a high temperature tube
furnace, Elmore, Huffman, and Wolf developed the following
general equations to describe defluorination of phosphate rock
as a resistance phenomena:

$$\frac{1}{K} = \frac{0.988d}{M} + \frac{0.359d^2}{D}$$

Where $\frac{1}{K}$ = total resistance to defluorination,

  d = depth of charge in cm.,

  M and D = constants for a given composition at con-
    stant temperature and conditions in the
    furnace atmosphere,

  $\frac{0.988d}{M}$ = resistance to defluorination at the surface,

  $\frac{0.359d^2}{D}$ = resistance to defluorination due to diffu-
    sion in the melt.

Defluorination of phosphate rock can be obtained by
the passage of steam and sulfur dioxide gas over the rock
during calcination. The sulfur dioxide probably displaces the
fluorine in the fluorapatite and the presence of steam results
in the formation of hydrogen fluoride. The hydrogen fluoride,
regardless of the sweeping action of the gas stream would react
with the silica in the rock to form silicon tetrafluoride. The

probable reactions taking place at 1000°C are shown in the
following simplified equations:

$$CaF_2 + H_2O + SO_2 = CaSO_3 + 2HF$$

$$4HF + SiO_2 = SiF_4 + 2H_2O$$

In this method of defluorination of phosphate rock,
as in practically all of the other methods, tricalcium phosphate
is formed, which is a source of readily available phosphorus.

Trisodium phosphate, Na_3PO_4, is the most widely used
compound of the phosphates. Its method of preparation is
carried out in two steps. Sodium carbonate is treated with
phosphoric acid to yield disodium phosphate. The disodium
phosphate is treated with sodium hydroxide to give trisodium
phosphate. These reactions are shown in the following equations:

$$Na_2CO_3 + H_3PO_4 = Na_2HPO_4 + CO_2 + H_2O$$

$$Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O$$
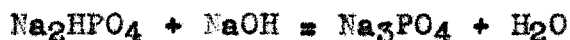
Proposed processes for trisodium phosphate manufacture
include a thermal one, in which soda ash or caustic soda is
fused with apatite; and also a wet process, in which finely
ground apatite is lixiviated with caustic liquors. Trisodium
phosphate has also been produced by sintering, in a rotary kiln,
a mixture of finely ground ferrophosphorus and soda ash in the
presence of air. The soluble trisodium phosphate is removed
from the sinter by leaching with water.

Sodium salts of meta- and pyrophosphoric acid have
been produced and for the most part can be looked upon as
molecularly dehydrated forms of the sodium orthophosphates.

Sodium metaphosphate can be prepared by any one of the following reactions:

$$NaH_2PO_4 + Heat = NaPO_3 + H_2O$$

$$Na_3PO_4 + P_2O_5 = 3NaPO_3$$

$$NaCl + HPO_3 = NaPO_3 + HCl$$
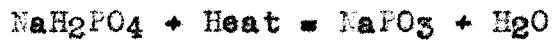
Sodium pyrophosphate is prepared by heating disodium phosphate as shown in the following reaction:

$$2Na_2HPO_4 + Heat = Na_4P_2O_7 + H_2O$$
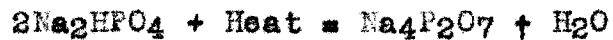
Converting the phosphates present in phosphate rock to phosphates of sodium would result in a method of easily extracting phosphorus from the rock.

E X P E R I M E N T A L

The purpose of the experimental work performed as part of this investigation is the reclamation of phosphorus from unwashed, low grade phosphate rock. Methods for the production of phosphoric acid, phosphate chemicals, and defluorinated phosphate rock are developed.

The phosphate rock used in this investigation is a Tennessee brown rock which has been ground to a fineness of minus 100 mesh. The rock received no treatment after being mined, other than that of drying and grinding, and was obtained at Ridley, Tennessee. This rock is identified as "No. 20 Rock". Its analysis is given in Table IV. In this table is also given the sulfuric acid requirements based on the amounts of calcium, iron, and aluminum oxide present. The "stoichiometric" or "theoretical" amounts of sulfuric acid required to give complete reaction is shown as 77.25 grams per 100 grams of rock.

Two methods, "volumetric" and spectrophotometric, were employed for phosphorus analysis. In most instances, analyses were made by both methods. Designation is made in the presentation of the data as to the methods used.

The volumetric procedure consists essentially of first precipitating the dissolved phosphates as ammonium phosphomolybdate, after which the precipitate is dissolved in a standard caustic solution. The excess caustic is then titrated with a standard acid solution. The phosphorus percentage, reported as P_2O_5, is calculated from the volumes of standard solution used. A complete detailed description of this method

TABLE IV.   ANALYSIS OF PHOSPHATE ROCK NO. 20

A. Rock Analysis:*

	Wet Basis (%)	Dry Basis (%)
Moisture	1.51	-
Ignition loss	5.31	5.39
CaO	19.15	19.48
P_2O_5**	15.50	15.75
Fe_2O_3	9.75	9.90
Al_2O_3	8.93	9.06
F	1.62	1.65
Acid Insoluble (SiO_2)	38.10	38.64
Total	99.87	99.87

   * As analyzed basis
   ** Volumetric method

B. Sulfuric Acid Requirements for Phosphoric Acid for 100 Grams
   Rock, 1.51% Moisture:

Constituents	H_2SO_4 Required (g.)
CaO	33.60
Al_2O_3	25.70
Fe_2O_3	17.95
Total	77.25

C. Proximate Rock Analysis (Dry Basis):

	Per Cent
$CaCO_3$	11.93
Apatite	23.61
$AlPO_4$	11.86
Al_2O_3*	4.05
Fe_2O_3*	9.90
Acid Insoluble (SiO_2)	38.65
Total	100.00

   * Combined as silicates

may be found in "Official and Tentative Methods of Analysis of
the Association of Official Agricultural Chemists" (33).

In the spectrophotometric method, the sample to be
analyzed is dissolved and reacted with a solution containing
sodium molybdate and hydrazine sulfate to form heteropoly com-
plex compounds of phosphorus. The heteropoly complex compounds
are reduced, resulting in a blue-colored solution. The trans-
mittancy of the solution was determined in a Beckman Model DU
spectrophotometer. From the per cent of light transmitted
through the solution, the per cent of the phosphorus can be
calculated (34).

The method used to analyze for iron and aluminum is
completely described in "Commercial Methods of Analysis" by
Snell and Biffen (35). The method consists essentially of
precipitating iron and aluminum as the phosphate in the presence
of ammonium acetate and acetic acid. The precipitate is trans-
ferred to a weighed crucible and ignited to the pyrophosphate
and weighed. The pyrophosphates are fused with sodium carbonate
and the melt dissolved in sulfuric acid. This solution is then
passed through a Jones reductor and titrated with standard
potassium permanganate. The amount of iron and aluminum can
then be calculated from the weights of pyrophosphates and the
volume of potassium permanganate used.

The analyses for fluorine were made by adding sul-
furic acid and silica to the sample and steam distilling.
The fluorine is volatilized as H_2SiF_6 and collected in the

distillate. The distillate is titrated with a standard thorium nitrate solution, using zirconium alizarin sulfonate as an indicator. The per cent fluorine is then calculated from the amount of thorium nitrate used for titration (36).

Work on the production of phosphoric acid from phosphate rock was performed by leaching 100 grams of rock with acid. The general procedure followed in all leaching runs was to place the desired amount of acid in a 600 milliliter beaker and add the weighed amount of rock to the acid with agitation. The mixture was stirred continuously throughout the run (4 hours) by means of an electric stirrer. After four hours, the unreacted rock was filtered off by vacuum filtration and washed with water. The unreacted rock was analyzed for phosphorus. The filtrate (crude phosphoric acid) was analyzed for phosphorus, iron, and aluminum.

The first series of leaching runs made were exploratory in nature and were made to determine the relative merits of sulfuric and nitric acids as leaching agents. Runs 101, 102, and 107 were made using a 20 per cent P_2O_5, unwashed rock (No. 2U) as this was the only rock available at the time. Nitric acid was used in runs 101 and 102 and sulfuric acid was used in runs 107 and 109. The rock used in run 109 was "No. 20 Rock" containing 15.5% P_2O_5. Equivalent amounts of acids were used in all cases. In these four runs analyses were only made for phosphorus, reported as P_2O_5. From the results obtained, as shown in Table V, nitric acid offered no advantage over

TABLE V. EXPLORATORY RUNS WITH NITRIC AND SULFURIC ACID

Run No.	101	102	107	109
Rock: No.	2U	2U	2U	20
Wt. (g.)	100	100	100	100
P_2O_5 (%)	20.0	20.0	20.0	15.5
Acid: Kind	HNO_3	HNO_3	H_2SO_4	H_2SO_4
Conc. (°Be')	25.0	30.0	22.8	35.0
Conc. (%)	35.0	42.0	26.0	41.3
Wt. (g.)	335.0	270.0	269.0	187.0
Theoretical (%)	100	100	100	100
P_2O_5 Extracted: Grams	10.80	17.25	14.45	13.24
%	54.00	86.20	72.25	85.50

sulfuric acid. Since sulfuric acid was the less expensive of the two, it was decided to use sulfuric acid in all the leaching runs that follow.

Following the decision to use sulfuric acid for leaching, a series of runs were made to determine the optimum concentration and amount of sulfuric acid to be used. A review of the data tabulated in Table VI shows variations in the total amounts (amount in filtrate plus amount of residue) of phosphorus, iron, and aluminum. After checking and rechecking the analysis, it was found that these variations were due to the non-uniformity of the rock as used. The two methods of analysis used, volumetric and spectrophotometric, check fairly well in analyzing the filtrate. The results obtained by the spectrophotometric method are slightly lower than by the volumetric method, the latter being affected by the large sulfate concentration. In the residue analysis, a larger variation is obtained with the two methods, the volumetric method giving higher results. This is due to the larger percentage of silica present in the residue. The spectrometric method is considered to be more accurate as this method is not subject to as many possible sources of interference as is the volumetric method.

Varying the concentrations of acid from 35° to 50°Be' and the amounts of acid between 90 and 132 per cent of theoretical required had no appreciable effect on the amount of phosphorus removed from the rock. There was a difference of approximately 10 per cent in the amounts of iron and aluminum extracted. The amount of iron and aluminum extracted was

TABLE VI. DETERMINATION OF OPTIMUM CONCENTRATION AND AMOUNTS OF SULFURIC ACID

Run No.	110	111	112	113	114
Sulfuric Acid:					
Conc. ($^{\circ}$Be')	22.8	35.0	35.0	50.0	50.0
Conc. (%)	26.0	41.3	41.3	62.2	62.2
Wt. (g.)	297.0	246.5	187.0	124.0	112.5
Theor. (%)	100	132	100	100	90
Wt. of Residue (g.)	107.7	106.5	108.3	106.9	107.0
Filtrate: Vol. (ml.)	575	360	387	438	400
Wt. (g.)	622.6	414.5	432.3	485.5	437.7
Sp. Gr.	1.090	1.173	1.133	1.119	1.120
P_2O_5 Analysis (Vol.)(g.):					
Filtrate	12.40	13.28	14.07	14.13	14.24
Residue	6.72	3.31	2.47	2.89	2.76
Total	19.12	16.59	17.04	17.02	17.00
P_2O_5 Extracted (%)	64.8	80.0	82.5	83.0	83.8
P_2O_5 Anal. (Spect.)(g.):					
Filtrate	12.22	13.30	13.24	13.65	13.68
Residue	5.41	2.21	1.94	1.87	2.27
Total	17.63	15.51	15.23	15.52	15.95
P_2O_5 Extracted (%)	69.3	85.7	87.0	88.0	85.8
Fe_2O_3 Analysis (g.):					
Filtrate	4.10	4.58	4.63	4.62	3.96
Residue	4.58	4.11	4.35	4.42	4.55
Total	8.68	8.69	8.98	9.04	8.51
Fe_2O_3 Extracted (%)	47.2	52.8	51.5	51.7	43.4
Al_2O_3 Analysis (g.):					
Filtrate	4.26	5.27	5.73	4.21	4.03
Residue	4.60	4.16	4.50	4.74	5.08
Total	8.86	9.43	10.23	8.95	9.11
Al_2O_3 Extracted (%)	48.1	35.9	56.0	47.1	44.2

Note: For all runs, 100 g. No. 20 rock used,
Temperature 20-25°C,
Time 4 hours

approximately 50 per cent of the original amounts in the rock.
The change of 10 per cent at this high percentage in the amount
extracted does not alter the problem of iron and aluminum
removal to any extent. In view of this, the percentage iron
and aluminum extracted was considered of secondary importance
in determining the optimum amount and concentration of sulfuric
acid to be used. Using concentrations of sulfuric acid above
50°Be' did not give sufficient fluidity to the mix to give
complete reaction. Because of this decrease in fluidity at
higher concentrations, the lower concentrations were considered
the most generally satisfactory.

In the runs presented in Table VI, difficulties were
experienced in filtering the mix. A series of runs were made
to determine the effect of temperature on the filtering charac-
teristics of the mix and the general behavior of the reaction.
A temperature of 75°C was used for these runs to assist in
gypsum crystal growth. This temperature was taken as an upper
limit, because at temperatures of 100°C and above, gypsum dehy-
drates. The dehydration of gypsum to form anhydrite would
increase filtering difficulties. A constant temperature was
maintained by placing the beaker in which the reaction took
place in a constant temperature bath. A study was also made
in these runs to determine the maximum concentration of phos-
phorus obtainable in the filtrate at maximum extraction. Where
varying concentrations and amounts of acid were employed, the
volume of the final filtrate (crude phosphoric acid) and not

the volume of wash water used, must be used as a criteria.

The filtering rate was slightly improved due to the agglomeration of calcium sulfate at a reaction temperature of 75°C. A review of the results in Table VII shows that the temperature does not affect appreciably the extraction of phosphorus from phosphate rock (Run 115).

Run 116 was made, using only the sulfuric acid requirements for reaction with CaO and Al_2O_3 (59.3 grams of 100% sulfuric acid) to determine if preferential reaction would take place. The amount of iron extracted was essentially the same as in runs using 100% of theoretical amount (77.3 grams of 100% sulfuric acid) of sulfuric acid.

A study of the results obtained to this point revealed that varying the conditions of leaching slightly improved filtering conditions but did not lower the per cent of iron and aluminum extracted. Two methods were tried to remove the impurities (iron and aluminum) appearing in the crude phosphoric acid. The first method was the usual method used for removal of iron and aluminum from phosphoric acid; i.e., pH adjustment. From the results shown in Table VIII, it can be seen that all the iron and aluminum was removed from solution as the phosphate. Since such high percentages of iron and aluminum are present in solution, their precipitation as the phosphates leaves very little phosphorus in solution. This method is not a feasible way to remove iron and aluminum.

The second method, electrodeposition, was used to

TABLE VII. SULFURIC ACID LEACHING AT 75°C

Run No.	115	116	117
Sulfuric Acid:			
Conc. (°Be')	50	30	30
Conc. (%)	62.2	34.6	34.6
Wt. (g.)	124.0	172.0	222.0
Theoretical (%)	100.0	77.0	100.0
Wt. of Residue (g.)	115.1	113.1	125.1
Vol. of Filtrate (ml.)	285.0	112.4	98.5
P_2O_5 Analysis (g.)(Volumetric):			
Filtrate	16.31	9.00	7.60
Residue	3.03	7.73	9.90
Total	19.34	16.73	17.50
P_2O_5 Extracted (%)	84.4	53.8	43.4
P_2O_5 Analysis (g.)(Spectro.):			
Filtrate	15.52	8.93	7.18
Residue	2.18		
Total	17.70		
P_2O_5 Extracted (%)	87.80		
Fe_2O_3 Analysis (g.):			
Filtrate	7.44	4.22	
Residue	2.42	4.46	
Total	9.86	8.68	
Fe_2O_3 Extracted (%)	75.40	48.60	
Al_2O_3 Analysis (g.):			
Filtrate	7.87	4.54	
Residue	1.66	5.30	
Total	9.53	9.84	
Al_2O_3 Extracted (%)	82.60	46.10	

TABLE VIII.   IRON AND ALUMINUM REMOVAL BY pH ADJUSTMENT

Run No.	110-P
Ml. taken from Run 110 filtrate for treatment	100
*P_2O_5 in filtrate (g.)	2.345
pH of filtrate	<1
pH at which precipitate first formed	1-2
Ml. 10% solution of Na_2CO_3 added to raise pH to 4.5	107
Weight of precipitate (g.)	5.5
Volume of filtrate (ml.)	207
Fe_2O_3 in filtrate (g.)	Tr.
Al_2O_3 in filtrate (g.)	Tr.
Al_2O_3 and Fe_2O_3 precipitated (%)	99+
P_2O_5 remaining in solution (%)	10.12

* Based on original volume of filtrate in Run 110 - 575 ml.
  Spectrophotometric method used.

remove only the iron from solution. A moderate current density was employed and both iron and aluminum cathodes were used separately. A source of direct current was obtained from a six volt battery, using a variable resistor to maintain the desired amperage. Removal of iron should result in an increase in weight of the cathode. Table IX shows that, essentially, no weight change of the cathode occurred; hence no iron was removed from the solution.

No chemical method could be found or developed for the separation of iron and aluminum from phosphorus when the three occur in the proportions obtained in the filtrates. In view of this, tests were made to determine the effects of pre-treating the rock before leaching. These tests were also made to further ameliorate filtering conditions. Calcination offered a relatively inexpensive and simple method of pretreatment. The rock was calcined in a muffle furnace at 900-1000°C, and resulted in a 7.8 per cent decrease in weight. It was found, as shown in Table X, that calcining the rock before treating with acid not only cut down on the iron extracted but also changed the nature of the precipitate in such a manner that filtration was very rapid. The concentration of sulfuric acid used was 30°Be' which gave a mix having fluidity of a highly satisfactory nature, Numerically in milliliters the volume of filtrate was approximately twice the weight in grams of the residue. Optimum extraction and concentration of phosphorus were obtained under these conditions.

TABLE IX.   REMOVAL OF IRON BY ELECTRODEPOSITION

	Iron Cathode	Aluminum Cathode
Current Density (amps/sq. ft.)	20	20
Anode	Lead	Lead
Current used (amps.)	2.93	1.18
Time of Plating (min.)	30	30
Initial weight of cathode (g.)	26.6821	6.0374
Weight of cathode after plating	26.6742	6.0324

Note: Filtrate from Run 114 used.

TABLE X.   LEACHING OF CALCINED NO. 20 ROCK WITH H_2SO_4

Run No.	118
Initial weight of rock (g.)	100.0
Calcining Temperature (°C)	900-1000
Calcining Time (hrs.)	3
Weight of rock after calcining (g.)	92.2
Weight of H_2SO_4 used for leaching (g.)	222.0
Concentration of H_2SO_4 (°Be')	30
Time of leaching (hrs.)	4
Temperature of leaching (°C)	75
Volume of Filtrate (ml.)	200
Weight of residue (g.)	108.3
P_2O_5 Analysis (g.): Residue*	2.35
Filtrate*	11.16
Total	13.51
P_2O_5 Extracted (%)	82.50
Fe_2O_3 Analysis (g.): Residue	5.01
Filtrate	3.02
Total	8.03
Fe_2O_3 Extracted (%)	37.60
Al_2O_3 Analysis (g.): Residue	3.57
Filtrate	3.07
Total	6.64
Al_2O_3 Extracted (%)	53.75

* Spectrophotometric Method

The concentrations of the crude phosphoric acid as obtained in the filtrate was between 5 and 10 per cent P_2O_5. A series of tests were made to determine to what strength the crude phosphoric acid could be concentrated. Concentration was carried on by evaporation, not allowing the temperature to exceed 150°C at any time. At temperatures above 150°C, the orthophosphoric acid is converted to pyrophosphoric acid. The results of these concentration tests are shown in Table XI. For these tests, 1000 grams of rock were leached with slightly less than the theoretical amount of 30° Be' sulfuric acid, to produce the crude phosphoric acid.

Crude phosphoric acid can be concentrated to 25 per cent H_3PO_4 by evaporation of water at temperatures below 150°C. No evaporation takes place at or below temperatures of 150°C when the strength of the acid reaches 25 per cent H_3PO_4. During concentration iron and aluminum phosphates crystallized out according to their solubilities in phosphoric acid.

The data shown in Table XI bears out the conclusion that maximum extraction of phosphorus from the rock is not obtained unless the volume (in ml.) filtered is substantially greater than the weight (in grams) of the residue. It is of interest to note that, in spite of the differences in amounts of phosphorus extracted, the concentration of phosphorus in the filtrate is essentially the same.

Since the crude phosphoric acid obtained by sulfuric acid leaching of rock contained relatively large amounts of

TABLE XI.   CONCENTRATION OF CRUDE PHOSPHORIC ACID

Leaching	Run 127	Run 133
Initial weight of No. 20 rock (g.)	1000	1000
Calcination Temperature ($^{\circ}$C)	900-1000	900-1000
Calcination Time (hrs.)	3	3
Weight of rock after calcination (g.)	922	922
Weight of 30° Be' H_2SO_4 (g.)	2000	2000
Temperature of Leaching ($^{\circ}$C)	75	75
Weight of Filtrate (g.)	1072	1450
Volume of Filtrate (ml.)	825	1132
Weight of Residue (g.)	1012	1015
Weight of P_2O_5 in Filtrate (g.)[1]	78.6	101.88
P_2O_5 Extracted (%)[2]	52.5	67.8
P_2O_5 in Filtrate (%)[3]	7.33	7.02
Concentration		
Volume of Filtrate after Conc. (ml.)	142	143
Weight of Filtrate after Conc. (g.)	252	263
Weight of P_2O_5 in Conc. Filtrate (g.)[1]	45.44	47.7
P_2O_5 in Conc. Filtrate (%)[3]	18.00	18.15
H_3PO_4 in Conc. Filtrate (%)[3]	24.85	25.05

(1) By Spectrophotometric Method
(2) Based on 15.5% P_2O_5 content of rock
(3) Weight basis

iron and aluminum, a possibility of producing iron or aluminum phosphate from the crude acid existed. The crude phosphoric acid was saturated with iron filings in an attempt to bring down a relatively pure iron phosphate. The same procedure was used with aluminum powder in an attempt to bring down aluminum phosphate. Any phosphates which would be precipitated would be reflected by a decrease of phosphorus in the solution. The results of four runs are tabulated in Table XII, and show that iron or aluminum phosphates cannot be produced in this manner.

Leachings of phosphate rock were made with solutions of sodium hydroxide and sodium carbonate to produce sodium phosphate directly from the rock. The procedure followed was the same as that in making sulfuric acid leachings. Calcined rock was used. As can readily be seen from the data in Table XIII, this process offers no promise whatsoever.

A second method of forming sodium phosphate was tried. This method consists of fusing phosphate rock with sodium salts or with sodium hydroxide. The fused mass was ground and then leached with water to remove the water soluble sodium phosphates formed. The insolubles were then filtered off and the leach liquor analyzed for phosphorus. The results of these fusions are shown in Table XIV. Fusing phosphate rock with sodium carbonate and with sodium hydroxide does show some promise for producing sodium phosphates, but the economy of this process when such low extractions are obtained makes its practicability highly questionable.

TABLE XII. FORMATION OF IRON AND ALUMINUM PHOSPHATES

	Run 131	Run 136	Run 132	Run 135
Volume of solution used (ml.)	100	50	100	50
P_2O_5 originally in solution (g.)	3.12	1.71	3.12	1.71
Weight of Iron added (g.)	1.28	2.00		
Weight of Aluminum added (g.)			1.79	2.00
P_2O_5 remaining in solution (g.)*	3.05	1.68	3.15	1.82

* By Spectrophotometric Method

TABLE XIII. LEACHING OF PHOSPHATE ROCK WITH SOLUTIONS
OF NAOH AND NACO$_3$

	Run 119	Run 128	Run 120	Run 121
Initial Weight of Rock (g.)	50	100	50	50
Leaching Agent	NaOH	NaOH	Na$_2$CO$_3$	Na$_2$CO$_3$
Wt. of Leaching Agent 100% (g.)	8.5	36.6	16.5	33
Vol. of Leaching Agent (ml.)	50	130	136	272
Str. of Leaching Solution (%)	15	22.5	10	10
% of Theoretical Required[a]	65	137	100	200
Temperature of Leaching (°C)	20-25	20-25	75	75
Time of Leaching (hrs.)	4	4	4	4
Wt. of Residue (g.)	48.1		48.0	46
Vol. of Filtrate (ml.)	244	303	207	304
P$_2$O$_5$ in Filtrate (g.)	0.823[b]	2.06[c]	0.178[b]	0.146[b]
P$_2$O$_5$ Extracted[d] (%)	10.6	13.30	2.95	1.88

(a) Calc. as amount necessary to convert P$_2$O$_5$ in rock to Na$_3$PO$_4$
(b) By Volumetric Method
(c) By Spectrophotometric Method
(d) Based on 15.5% P$_2$O$_5$ in Rock

TABLE XIV. NaOH, NaCl, Na_2CO_3 and Na_2SO_4 FUSIONS OF PHOSPHATE ROCK

	Na_2CO_3 Run 122	Na_2CO_3 Run 124	Na_2SO_4 Run 125	NaCl Run 126	NaOH Run 129
Wt. of Rock (g.)	10	10	10	10	20
Time of Fusion (hrs.)	1	1	1	1	2
Wt. of Fusing Agent (g.)	5	10	10	10	7.32
Vol. of H_2O used for Leaching (ml.)	100	100	100	100	130
Temp. of Leaching ($^{\circ}C$)	75	75	75	75	75
Wt. of P_2O_5 in Leach Liquor (g.)	0.305[a]	0.452[a]	Trace	None	0.802[b]
P_2O_5 Extracted from Rock (%)[c]	19.2	29.2	—	0	25.8

Note: Temperature of fusion 950-1000°C.

(a) By Volumetric Method
(b) By Spectrophotometric Method
(c) Based on 15.5% P_2O_5 in Rock

Defluorinated phosphate rock was produced by heating a mixture of phosphate rock and sulfur. Two methods were used for defluorination. The first method, used in runs 106 and 108 in Table XV, consists of putting a mixture of sulfur and rock in a crucible and heating to 1000°C for one to three hours.

The second method, used in runs 134, 137, and 139 in Table XV, employs the "flash roasting" principle. The rock-sulfur mixture is injected into the center of a gas flame by introducing the mixture into the burner with the primary air. This method does not give as complete defluorination of the rock as does the first method, the reason being that a flame temperature above 750°C could not be obtained. There is every indication to believe that at comparable temperatures, the "flash roasting" method would be superior to the crucible method. An added advantage of the flash roasting method is the short time needed for defluorination. Both of these methods will produce a rock containing less than one per cent fluorine.

TABLE XV.   DEFLUORINATION OF PHOSPHATE ROCK

	Run 106-A	Run 106-B	Run 108-A	Run 108-B	Run 134-A	Run 134-B	Run 137-A	Run 137-B	Run 139-A	Run 139-B
Wt. of Rock (g.)	20	20	20	20	50	50	50	50	50	50
No. of Rock	2U	2U	2U	2U	20	20	F3	F3	2U	2U
Fluorine in Rock Orig.(%)	6.21	6.21	6.21	6.21	1.63	1.63	3.71	3.71	6.21	6.21
Wt. of Sulfur (g.)	1	1	2	2	1	2.5	1	2.5	1	2.5
Sulfur in Mix. (%)	5	5	10	10	2	5	2	5	2	5
Temp. Muffle Furnace (°C)	1000	1000	1000	1000						
Temp. Burner Flame (°C)					700-750	700-750	700-750	700-750	700-750	700-750
Time of Run (Mins.)	180	60	60	180	15	20	15	15	15	15
Fluorine Rem. in Rock (%)	1.780	0.741	0.801	1.24	1.02	0.55	1.40	1.36	2.20	1.40

S U M M A R Y

Leaching of unwashed, low grade, Tennessee brown phosphate rock with sulfuric acid yielded a phosphoric acid which could be concentrated to 25 per cent H_3PO_4. Pretreating the rock by calcination at 900-1000°C before acidulation resulted in a depression of the amount of iron extracted and also increased the rate of filtration.

The phosphate rock was ground to a fineness of at least 100 mesh. This fineness insured intimate contact between the acid and the rock.

Chemically, temperature had no appreciable effect on the nature of the reaction between phosphate rock. Temperature did influence the reaction physically. If the reaction took place at temperatures below 50°C, the calcium sulfate was in the form of very fine crystals that were difficult to filter. Temperatures of approximately 75°C caused agglomeration of the calcium sulfate which facilitated filtration. Temperatures of approximately 100°C dehydrated gypsum so that there was an increase in filtering difficulties.

The strength of the required sulfuric acid was influenced by the resulting fluidity of the mix. This did not present a problem with higher grades of rock, as in commercial production, since the ratio of solids to liquor was much lower. In the reaction between the dry rock and stoichiometric amounts of sulfuric acid, the acid had to be diluted to at least 50°Be'. For a reaction time of four hours, varying the concentration of sulfuric acid between 30 and 50°Be', did not effect the

amount of phosphorus extracted, phosphoric acid formed, from the rock. The higher the concentration of sulfuric acid used, the more wash water needed to completely wash the extracted phosphorus out of the unreacted rock. Using stoichiometric amounts of sulfuric acid below $30^\circ Be'$, resulted in a decrease in the amount of phosphorus extracted. The optimum concentration of sulfuric acid for leaching of phosphate rock was $30^\circ Be'$.

It was found essential for maximum extraction that the volume (in ml.) of filtrate obtained be twice as great as the weight (in grams) of the residue. The weight of the residue obtained from all leachings was practically constant - being 5 to 10 per cent greater than the weight of the original rock used.

The concentration of phosphoric acid as obtained from leaching was 5-10 per cent, but could be increased to 25 per cent by evaporation of water. This phosphoric acid could possibly be used for acidulation of phosphate rock to produce a phosphate fertilizer having a higher phosphorus content than ordinary superphosphate. The presence of iron and aluminum as impurities in the phosphoric acid presented a major problem since both impurities form insoluble phosphates that are unavailable to plant life in fertilizers.

Fusing phosphate rock with sodium carbonate and sodium hydroxide converted 25 per cent of the P_2O_5 in the rock to the water soluble form. The use of sodium chloride

and sodium sulfate as fusing agents yielded no water soluble phosphate.

Leachings of phosphate rock were performed with sodium carbonate or sodium hydroxide solution in a manner similar to that used for sulfuric acid. These leachings gave only small extractions of phosphorus from the rock.

Defluorination of phosphate rock was carried out with two methods, crucible and flash roasting. Both methods yielded a phosphate rock containing less than one per cent fluorine. Better results were obtained in the crucible method, in which the temperature used is 1000°C, in comparison with 750°C used in the flash roasting method. Under comparable temperature conditions, there was strong indication of the superiority of the flash roasting method. This method required a much shorter reaction time than the crucible method.

LITERATURE CITED

(1) Grey, A. N., "Phosphates and Superphosphates", p. 126, London, Interscience Publishers (1942).

(2) Meckstroth, J. T., Chem. and Met. Eng., 26, 77-79 (1922).

(3) Larison, E. L., Ind. Eng. Chem., 21, 1172-5 (1929).

(4) Klugh, B. G., Chem. and Met. Eng., 36, 666 (1928).

(5) Hignett, T. P., Chem. Eng. Progress, 44, 753-64, 821-32, 895-904 (1948).

(6) Jacob, K. D., Ind. Eng. Chem., 23, 14-21 (1931).

(7) Mansfield, G. R., Ind. Eng. Chem., 34, 9 (1934).

(8) Mineral's Yearbook, 1945, United States Government Printing Office (1947) p. 1393.

(9) Meyer, Ernst Von, "A History of Chemistry", 3rd edition, p. 156. London, McMillan and Co., Ltd. (1910).

(10) Kirkpatrick, S. D., Chem. and Met. Eng., 44, 644-9 (1937).

(11) Roscoe, H. E., and Schorlemmer, E., "A Treatise on Chemistry", Vol. I, 4th edition, p. 613, London, McMillan and Co., Ltd. (1911).

(12) Carothers, J. N., Chem. Ind., 42, 523, 525, 527-8 (1938).

(13) Carothers, J. N., J. Ind. Eng. Chem. 10, 35, 329 (1918).

(14) Carothers, J. N., Ind. Eng. Chem., 9, 26 (1917).

(15) Waggaman, W. H., Easterwood, H. W., and Turley, T. B., U. S. Dept. Agr., Bull. 1178, 53 pp. (1923).

(16) Weber, W. C., Shafer, R. W., and Roberts, E. J., U. S. Patent No. 2,049,032 (1936).

(17) Shreve, R. Norris, "Chemical Process Industries", pp. 337-45. New York, McGraw-Hill Book Co. (1945).

(18) Curtiss, H. A., Trans. Am. Inst. Chem. Eng., 31, 278-95 (1935).

(19) Badger, W. L., and Baker, E. M., "Inorganic Chemical Technology", 2nd edition, pp. 127-33. New York, McGraw-Hill Book Co. (1941).

(20) Easterwood, H. W., Ind. Eng. Chem., 24, 9-19 (1942).

(21) Hall, R. E., U. S. Patent No. 1,956,515 (1934).

(22) Frazer, H. F., Hoppe, T. C., Sullivan, J. H., and Smith, E. R., Ind. Eng. Chem., 35, 1087-90 (1943).

(23) Fox, E. J., and Hill, W. L., Ind. Eng. Chem., 38, 329-34 (1946).

(24) Elmore, K. L., U. S. Patent No. 2,368,649 (1945).

(25) Elmore, K. L., Huffman, E. C., and Wolf, W. W., Ind. Eng. Chem., 34, 40-48 (1942).

(26) Curtiss, H. A., and Miller, A. M., Chem. and Met. Eng., 43, 408 (1938).

(27) Curtiss, H. A., Miller, A. M., and Junkins, Chemical and Met. Eng., 43, 583-87 (1936).

(28) Copson, R. L., Newton, R. H., and Lindsay, J. D., Ind. Eng. Chem. 29, 175-9 (1937).

(29) Tyler, P. M., and Moseley, H. R., Am. Inst. Mech. Eng. Tech. Publication No. 1053, Mining Technology (1939).

(30) Miller, A. M., Mining and Met. 25, 492-4 (1924).

(31) Rogers, Allen, "Industrial Chemistry", 4th edition, p. 503. New York, D. Van Nostrand Co. (1925).

(32) Ries, H., and Watson, T. L., "Engineering Geology", 5th edition, p. 123. New York, John Wiley & Sons, Inc. (1936).

(33) "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemist," 6th edition, pp. 22-3. Washington, D. C., Association Agricultural Chemist (1945).

(34) Boltz, D. F., and Mellon, M. G., Ind. Eng. Chem., Anal. Ed., 19, 673-77 (1947).

(35) Snell, F. D., and Biffen, F. M., "Commercial Methods of Analysis", pp. 191-5, New York, McGraw-Hill Book Co., (1944).

(36) Willard, W. H., and Winter, O. D., Ind. Eng. Chem., Anal. Ed., 5, 7-10 (1933).

A P P E N D I X

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V I T A

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