An Investigation Into Methods Of Dressing Land Pebble Phosphate Rock With A View To Effecting A Greater Saving

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To the Graduate Council:

I am submitting herewith a thesis written by Russell De Costa Greene entitled "An Investigation Into Methods Of Dressing Land Pebble Phosphate Rock With A View To Effecting A Greater Saving." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Engineering Science.

, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
AN INVESTIGATION INTO METHODS OF DRESSING LAND PEBBLE PHOSPHATE ROCK WITH A VIEW TO EFFECTING A GREATER SAVING.

Submitted in partial fulfillment of the requirements for the degree of Engineer of Mines in the University of Tennessee,

by

Russell de Costa Greene

May 28th 1913.
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INTRODUCTION.

The object of the following investigation was to inquire into the present methods of separating land pebble phosphate rock from the sand and clay matrix in which it occurs with a view to effecting a greater recovery of values or, in the event of this proving impossible or impracticable, to devise an economical chemical treatment for the tailings containing these unrecovered values such that the product would be a salable one.

GEOLOGY AND OCCURRENCE OF FLORIDA PHOSPHATE DEPOSITS.

The geological formations of Florida include strata of Eocene, Miocene, Pliocene, Post-Pliocene and Recent periods. EOCENE. The rocks of this formation are chiefly white, gray, or yellowish limestones of porous texture and highly fossiliferous. The thickness of the formation varies between 300 and 500 feet. Along the median portion of the Eocene area with a north and south trend lie the heavy deposits of hard rock phosphates.

MIocene. This, like the Eocene, is a limestone formation but is distinctly bedded and comprises rocks of a more compact nature and less subject to disintegration. The Miocene phosphate area is confined to the northern and western part of the State. It directly overlies the Eocene.
PLIOCENE. This formation includes marls, clays and limestones and a unique phosphate deposit locally known as pebble rock with which our investigation is concerned. This is the most important class of phosphates. Its type locality is on headwaters of the Peace, Alafia and Manatee rivers. It is in general an unstratified bed of pebbles of phosphate of lime in a clay matrix. Both matrix and pebbles are normally white or gray in color. The matrix is soft, friable and pervious and when mined readily permits the separation of its contained pebbles by washing; the thickness is variable, the result of non-conformity of transportation of its material by erosive action and of causes connected with its mode of origin. The pebble contents amount to from 25-50% of the deposit. The formation rests unconformably upon both Eocene and Miocene formation.

RECENT. The deposits of this age include the superficial sands, the bodies of sand and gravel occupying the early river beds, which now underlie the bottom lands and the sands and phosphates gravels of the present channels.

Florida contains two general classes of commercial phosphate, each having a peculiar genesis, form of deposit and chemical and physical properties. These are known as "hard rock" and "land pebble".

HARD ROCK PHOSPHATE is a hard, massive rock of general appearance similar to limestone, precipitated from thermal springs. The rock contains irregular cavities usually lined with secondary incrustations of phosphate of lime. The fracture is angular.
The contents of phosphoric anhydride \( (\text{P}_2\text{O}_5) \) run slightly above or below 36.65%.

**Land Pebble Phosphate** consists as before noted, of pebbles of phosphate of lime varying in size and shape but normally of uniform texture, color and chemical contents. They vary in color from white to dark gray and almost black. The exterior is smooth and glassy. The pebbles are composed of an earthy material containing fossil remains, grains of quartz and pisolitic grains of lime phosphate. They range from minute size to that of an English walnut. The phosphoric anhydride averages about 32.06%.

The deteriorating constituents of all phosphates are chiefly the insoluble matters, the carbonate of lime and the oxides of iron and alumina. The percentage of \( \text{P}_2\text{O}_5 \) is generally in inverse ratio to the amount of insoluble matter chiefly sand.

The economical effect of the amount of insoluble matter is chiefly mechanical, adding to its weight, to the cost of transportation and handling. The second constituent, carbonate of lime, has in addition a chemical disability in that it takes up a certain amount of sulphuric acid in the manufacture of superphosphates.

The effect of oxides of iron and alumina is to cause an acid phosphate to revert with direct loss of \( \text{P}_2\text{O}_5 \) and to render the manufactured product moist and sticky and difficult to dry. Phosphate buyers therefore, limit the contents in Al...
Fe₂O₃ (Land A) to 4%, deducting for each unit of these constituents above this percentage, the equivalent in phosphate of lime which might become available from the P₂O₅ taken up by the Al₂Fe₂O₅.

Typical analyses of the land pebble phosphate are given in accompanying analyses of two samples, made by Dr. T.M. Chatard, Dir. of Chemistry, U.S. Geological Survey, which are taken as representing the limits of the rock at two ends of the series of graduations in variations in the amount of these several constituents especially their phosphoric anhydride.

The usual percentage of phosphate of lime is between 68 and 70.

Analysis #3 represents the matrix which held the pebble represented by analysis No. 1. The general run of the matrix represents the tailings in washing on a working scale and is probably representative of the lowest percentage to which it is thought economical to dress, wash and separate the two components of the deposit, the pebble and matrix.
#5.

## ANALYSIS OF TWO SAMPLES OF LAND PEBBLE PHOSPHATE

### ROCK AND ONE SAMPLE OF MATRIX.

<table>
<thead>
<tr>
<th></th>
<th>Pebble 1</th>
<th>Pebble 2</th>
<th>Matrix 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss (H₂O) at 105°C</td>
<td>0.63</td>
<td>0.79</td>
<td>3.34</td>
</tr>
<tr>
<td>&quot; red heat</td>
<td>3.15</td>
<td>3.47</td>
<td>6.38</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.19</td>
<td>3.93</td>
<td>0.82</td>
</tr>
<tr>
<td>F</td>
<td>2.72</td>
<td>1.86</td>
<td>0.88</td>
</tr>
<tr>
<td>Insol.residue (in HCl,HNO₃)</td>
<td>4.34</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>&quot;</td>
<td>6.69</td>
<td>49.78</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.53</td>
<td>2.14</td>
<td>6.35</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.35</td>
<td>0.61</td>
<td>1.05</td>
</tr>
<tr>
<td>CaO</td>
<td>47.95</td>
<td>46.03</td>
<td>15.92</td>
</tr>
<tr>
<td>MgO</td>
<td>0.21</td>
<td>0.33</td>
<td>0.37</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>34.72</td>
<td>31.50</td>
<td>13.58</td>
</tr>
</tbody>
</table>
METHODS OF MINING & DRESSING.

Hydraulic mining is practiced at all of the land pebble mines, the overburden being removed either by steam shovels or hydraulic picking.

The rock and matrix are undermined in the bank by a hydraulic giant and flow to a sump from which they are pumped by a centrifugal sand pump to the so called washers where a partial separation of the rock and matrix takes place.

The washer consists of one or two series of double shell revolving trommels and log washers with a crusher interpolated if necessary.

The impact of the water from the giants and action of the currents in the pipe line aids in the separation of the rock from the clay and sand.

The rock and matrix are discharged from the pump upon a flat screen usually 10 to 12 ft. long having 1" x 3/8" apertures.

The sand is usually present in grains smaller than 1/16 " diam, but sometimes occurs in large irregular particles of sandstone with a low degree of cohesion, called "sand rock". The presence of sand rock necessitates crushing. By this means the sand rock is reduced to the size of 1/4".

The oversize of the flat screen passes into a 36" x 6' rotary screen called a separator, with 1-1/8 round holes. The object of this screen is to remove large balls of clay from the feed.
The undersize of this separator screen goes to the first double log washer and the oversize to waste.

The log washers are 21 ft. long and contain the separation of the rock from the matrix by subjecting them to the action of revolving blades having a pitch toward the discharge end of the log, at the same time the feed is subjected to the action of a current of clear water flowing counterclockwise to the travel of the feed and overflowing on one side at the feed end.

The result of the combined action is to effect a partial separation between the rock, clay and sand, the finer sizes of each being carried off in suspension to the overflow and from thence to waste.

The discharge from the head end of the logs then passes to a 48" x 6' double shell rotary rinsing screen having 5/8" round holes in the inner screen and 1 x 3/16" holes in the outer screen. The oversize of the inner screen goes to the washer, where one is used, otherwise it mixes with the undersize from the inner screen and falls into a second log washer. The undersize of the outer screen goes to waste.

After the feed leaves the second log washer it goes to a second double shell rotary screen. The oversize from both screens of this rotary screen falls into an elevator boot whence it is elevated to storage bins. The undersize of the
outer screen goes to waste. The apparatures in the second rotary are 3/8" round holes for the inner and 1" x 1/8" rectangular holes for the outer screen.

Shaking riddles have been substituted for the rotary screens in one plant but the practice generally is as outlined above.

The theory of the above method of treatment is that the economic values occur principally in the sizes larger than a 1/8" in diameter and that the sand occurs in the finer sizes.

This is only very approximately true as may be seen from the percentage of B.P.L. in analysis #3 of Dr. Chatard previously given. However, neglecting the high I & A. in this sample, the B. P. L. content is too low to make it a salable article, as 50% B.P.L. is the minimum percentage which is marketable at this time.

The present methods of washing may be seen then to consist in simple sizing.

The degree of recovery based on the total values is low as the following considerations will show. Assume the pebble shown in analysis #1 to constitute 30% of the pebble and matrix together. From 100 tons of pebble and matrix together we will then recover 30 tons of pebble analyzing

34.72 % $P_2O_5$ or 10.416 tons of $P_2O_5$. We will reject 70 tons of matrix shown by analysis #3 to contain 13.58 %
$P_2O_5$ or 9.506 tons of $P_2O_5$. The degree of recovery is 52.3%. However, the reject is unsalable.

Three possibilities now suggest themselves.

**FIRST:** To continue sizing to the point where the recovered product is merchantable.

**SECOND:** To subject the entire reject to a concentration process whereby the pebble and sand are separated sufficiently to make the product merchantable.

**THIRD:** To treat the reject chemically.

Resume of the Investigations of Others.

The first possibility has been experimented upon by the Palmetto Phosphate Co., who produced by the use of finer screens, a product, from their tailings, analyzing 55% B.P.P. They produced 1000 tons in this way but the difficulties experienced from screens and the fine material packing in their elevators and bins caused them to discontinue the treatment.

**Mechanical Concentration.**

The second possibility has been experimented upon on a laboratory scale by Dr. Thomas Wyatt, author of "Phosphate of America" who found the close similarity of the specific gravities of the rock and sand an insuperable obstacle to the cheap and effectual separation. If we except flotation and magnetic methods, applicable only to certain cases, all successful methods of ore dressing depend upon the differences in specific gravities between the economic mineral and the gangue.
The Armour Co. experimented also in this direction at their Florida plant but without success.

The third possibility that of chemical treatment:

CHEMICAL TREATMENT.

Mr. John Stewart of Ottawa, Canada, at the Baltimore meeting in Feb. 1892, of the Am. Inst. M.E. suggested a method of treatment of the low grade Laurentian ores from the Phosphate districts of Quebec and Ontario. The economic mineral consists of Apatite, hardness 5, sp. gr. 3.1 to 3.25 in a gangue of Pyroxene, hardness 5 to 6, sp. gr. 3.23 to 3.5 and Hornblende, hardness 5-6 and sp. gr. 2.9 to 3.4. It is evident that as in the case of the pebble rock of Florida, this ore cannot be successfully concentrated by crushing and jigging.

His process is a chemical one and proposes dropping the material in a finely divided state through a tower, the material being exposed to sulphurous and sulphuric acid vapors assisted by a water spray. He proposes to generate the sulphurous vapors required in kilns, by roasting the pyrite of this region. Nitric acid must be added to the water spray to convert the sulphur dioxide to sulphuric acid. The suggested reaction is as follows:

\[ 6 \text{SO}_2 + 4 \text{H}_2\text{O} + 4 \text{HNO}_3 = 6 \text{H}_2\text{SO}_4 + 4 \text{NO} \]
\[ 6\text{H}_2\text{SO}_4 + 4 \text{NO} + 3\text{Ca}_3\text{P}_2\text{O}_8 = 3\text{CaH}_4\text{P}_2\text{O}_8 + 6\text{CaSO}_4 + 4 \text{NO} \]  
(Insoluble)
Dr. Francis Wyatt of New York City in the discussion made the following criticism of the above plan, first: that it is extremely probable that an excess of $SO_2$ being present we would also have a soluble bisulphate of lime formed which, upon the application of the necessary heat to evaporate the solution containing both soluble salts, would be decomposed losing its sulphurous acid and its base combining with the phosphoric acid would cause the "mono" to be reverted to the insoluble bisulphate of lime.

second: Neglecting this possibility there is no doubt but that a considerable portion of the phosphates would escape all contact with the gases or acids and that the maximum recovery would not exceed 70%. On this basis Dr. Wyatt figures the cost of the process as follows:

2-1/2 tons 40% phosphate, mined and delivered at

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill at say $3.00 per ton</td>
<td>$7.50</td>
</tr>
<tr>
<td>Grinding 2-1/2 tons to a fineness of 100 mesh</td>
<td>3.00</td>
</tr>
<tr>
<td>1 ton of pyrite containing 35-40% S</td>
<td>3.50</td>
</tr>
<tr>
<td>100 lbs. Nitric acid used per ton of Apatite</td>
<td>5.00</td>
</tr>
<tr>
<td>Labor, fuel, interest, wear and tear of plant, etc.</td>
<td>2.00</td>
</tr>
<tr>
<td>Cost of treating 2-1/2 tons 40% Apatite ore-------------------------</td>
<td>$21.00</td>
</tr>
</tbody>
</table>

The evaporated solution will contain the equivalent of say 1,000 lbs. of crystallized mono-calcic phosphate which in a 40% solution costs $21.00

To evaporate to dryness 1.00

Packages, Rrt. and Chgs? at $4.00 per ton 2.00

Total cost of 1,000 lbs.--------------------- $24.00

Total cost per ton of 2240 lbs $53.76
This compound would contain 52-1/2 % \( P_2O_5 \) and would sell at about 80 cts. per unit and per gross ton. Its market value would consequently be 52.50 x .80 = $42. per ton, a loss of $11.76 or $4.75 per ton of the original low grade ore.

Dr. Wyatt suggests a method used in Europe. It consists in the manufacture of phosphoric acid in solution by means of weak oil of vitriol according to the equation

\[
Ca_3P_2O_8 + 3 H_2SO_4 = 3 CaSO_4 + 2 H_3PO_4
\]

This solution to be concentrated to 45° Beamsme.

The quantity of sulphuric acid of 50° Beamsme required for 2-1/2 tons of ore would be 4,000 lbs. The acid is then diluted to 14° Beamsme and mixed with the rock ground to fineness of 100 mesh. Two and 1/2 tons of ore will yield about 1900 lbs. of finished liquid of about 45° Beamsme. This will contain 45% or say 850 lbs. of \( P_2O_5 \).

He gives the cost of production as follows:

2-1/2 tons 40% phosphate mined and delivered at mill
at $3.00 per ton
Grinding 2-1/2 tons to fineness of 100 mesh
4000 lbs. chamber sulphuric acid of 50° Beamsme
at $5.00 per ton
Labor, fuel, wear and tear of plant
Cost of treating 2-1/2 tons 40% apatite ore and of producing 1900 lbs. 450 Beamsme phosphoric acid
Cost of 45° Beamsme phosphoric acid per ton of 2240#
Packages, frt. & Chgs. at $4. per ton
Total cost per ton

Actual market value is $1.00 per unit of \( P_2O_5 \) per gross ton. It is therefore worth $45. per ton and the com-
sequent profit on the 1900 lbs. produced from the 2-1/2 tons of raw material would be $12.30 or a little less than $5.00 per ton of low grade Apatite ore. These high grade "supers" have long been prepared in Europe. In their preparation the phosphoric acid replaces oil of vitriol as the solvent of the raw phosphates according to the equation:

\[ Ca_3 P_2 O_8 + 4 H_3 PO_4 = 3 CaH_4 P_2 O_8 \]

or

\[ 2 Ca_3 P_2 O_8 + 2 H_3 PO_4 = 3 Ca_2 H_2 P_2 O_8 \]

and the finished product contains from 40 to 45% of \( P_2 O_5 \) instead of 11-14% contained in the ordinary commercial article.

**SIZING TEST**

Through the courtesy of Mr. L. Warrington Gottman, Supt. of the Palmetto Phosphate Co. at Tiger Bay, Fla., I obtained two 150½ samples of land pebble tailings, representing the reject after washing the rock from the matrix.

I quartered one complete lot down to a sample weighing 100 grs. The results of sizing test of this material are given below:

<table>
<thead>
<tr>
<th>Apertures</th>
<th>MM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inches</td>
<td></td>
</tr>
<tr>
<td>On 10 mesh</td>
<td>2.41% by weight</td>
</tr>
<tr>
<td>20 ″</td>
<td>0.0041  2.136</td>
</tr>
<tr>
<td>40 ″</td>
<td>0.0081  0.970</td>
</tr>
<tr>
<td>60 ″</td>
<td>0.0165  0.420</td>
</tr>
<tr>
<td>80 ″</td>
<td>0.0102  0.250</td>
</tr>
<tr>
<td>100 ″</td>
<td>0.0063  0.160</td>
</tr>
<tr>
<td>Thru. 100 ″</td>
<td>3.69  99.52</td>
</tr>
</tbody>
</table>
METHOD OF ANALYSIS & ANALYSES.

As it was necessary to make a great number of determinations of bone phosphate of lime content, I decided to use a volumetric method which would be more rapid than a gravimetric one and equally accurate. The following method was adopted. It is the one used by the U.S. Government Experimental Stations and I am indebted for it to Mr. McIntyre of the Tennessee Station.

Take 2 gr. rock, add 25 cc. HCl Bail for one-half hour, cool and make up to 250 cc. volume. Take out 25 cc. with pipette. Put in a beaker and add 12 cc. NH₄OH acidulate with HNO₃ and heat to 65 °C; add 40 cc. NH₄MoO₄ and let ppt. stand 15 min. Filter rapidly, washing by decantation several times with cold water. Dissolve in measured quantity of standard KOH solution. Add 1/2 cc. of Phenolphthalein as indicator and titrate excess alkali with standard HNO₃ solution.

The Molybdate solution is made up as follows:

Take 100 gr. Molybdate acid, add 144 cc. ammonia (0.9 sp. gr.) and 271 cc. Water. Pour mixture into weak solution of Nitric acid containing 489 cc. Nitric sp. gr. 1.42, and 1146 cc. H₂O. 1 cc. of above solution will ppt. 1.4 mgms. P₂O₅.
The standard KOH solution is made up by taking 3233 cc. of a normal KOH solution and making it up to one liter with $H_2O$. 1 cc. is equivalent to 1 mg. $P_2O_5$.

The standard $HNO_3$ solution is made up by taking 161.9 cc. of a normal $HNO_3$ solution and making up to 1 liter with $H_2O$. Then 2 cc. stand. $HNO_3$ solution = 1 cc. stand KOH solution.

The Phenolphthalein solution contains 1 gr. of Phenolphthalein to 100 cc. of redistilled alcohol.

Analyses of samples retained on each size of screen mesh for $Ca_3P_2O_8$ (or bone phosphate of lime) gave the following results:

<table>
<thead>
<tr>
<th>Mesh</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>65.07</td>
</tr>
<tr>
<td>20</td>
<td>64.13</td>
</tr>
<tr>
<td>40</td>
<td>37.16</td>
</tr>
<tr>
<td>60</td>
<td>25.06</td>
</tr>
<tr>
<td>80</td>
<td>23.44</td>
</tr>
<tr>
<td>100</td>
<td>32.60</td>
</tr>
<tr>
<td>Through 100</td>
<td>28.28</td>
</tr>
</tbody>
</table>

DISCUSSION OF SIZING TEST & ANALYSES.

An inspection of the sizing test and above analyses showed that 73.2% of the whole sample was larger than 40 mesh, analyzing 47.53% B.P.I., and that 39.3% of the whole sample was larger than 60 mesh and analyzed 43.50 B.P.I.
It is apparent from an inspection of the results that the use of finer screens would result in the saving of large values, for example a 20 mesh screen would save 28.1% of the tailings without materially lowering the grade of the product.

On the basis of 30% pebble in the matrix and a pebble analyzing 66% B.P.I., the increase in tonnage would amount to 66% with an analysis of 66.5% B.P.I.

There is, however, a practical lower limit to screen sizing, probably 1/8", beyond which it is inadvisable to go, owing to blinding of the screens. It is on the other hand perfectly practical, and more economical than screening, to size hydraulically in a properly designed hydraulic classifier.

**HYDRAULIC CLASSIFICATION.**

This method is only suitable for the treatment of sizes below 3 mm. and could therefore only be successfully applied to the tailings or reject. I know of no instance where it has been applied to the treatment of phosphate rock in this country.

Mr. Henry Louis in his treatise "The Dressing of Minerals" on page 536 describes an ore dressing plant erected in Belgium, for the separation of soft earthy phosphate of lime from soft chalk and flints in which hydraulic classifiers
are successfully used to sort the feed for subsequent treatment on jigs. It has been demonstrated that fine sizing is desirable but the use of screens with smaller apertures than 1/8" is impracticable, expensive and in-effective. Hydraulic sizing has been successfully applied to a great variety of other ores where the sizes were so fine (below 3 mm.) as to make screening prohibitive.

Simple tests with rising currents of water in a long glass tube showed that the material is well adapted to this treatment.

**DESIGN OF 3 POCKET HYDRAULIC CLASSIFIER**

Design of 3 pocket Hydraulic Classifier to handle 100 tons in 24 hours. Spigot product to be all sizes larger than 0.420 mm. (on 40 mesh), all other sizes going into the overflow. From sizing test, overflow, = 25.23% of feed.

We will assume the tonnage per spigot per 24 hrs. at 25 tons. From the cumulative curve from sizing test, we find the size of the grains in each spigot to be as given on line 2 of Computation table appended. Line (3) Kgs per minute are computed from Line (1) by multiplying by 0.631. Line (4), the currents in mm/sec., are computed from the relation, \( \sqrt{V} = C \sqrt{D(s-1)} \), where \( V \) is the required velocity in mm/sec. \( C \), is a constant, equals 0.7, for quartz; \( D \),
equals diam. in mm. of the smallest quartz grain desired in any spigot; \( \xi \), equals specific gravity of the mineral; 2.61 to this case. The classifier will be designed for the lightest mineral, viz., the sand, as the heavier mineral will take care of itself. Line (5) equals Line (4) multiplied by 60. Assuming feed to be wholly quartz then Line (3) divided by 2.61 (sp. gr. of quartz) gives Line (6). Assuming feed will have 4 times as much water as ore by weight and that the rising water for any given sorting column will be 3 volumes of water to 1 vol. of sand, we multiply liters of sand by 3 to get liters of rising water per minute for each sorting column. Line (8) equals Line 6 plus Line 7. Line 9 equals Line 8 divided by Line 5 and multiplied by 1,000,000. Line (10) 

\[
\sqrt{\text{Line 4} \times \frac{\text{Line 9}}{\pi}}
\]

Line (11) gives the commercial size of pipe corresponding to Line (10), allowing a slight increase for friction. Line (12) is computed for spigot #1 by adding to the total water and sand given on Line 8 for the feed, the water rising in spigot 1, and subtracting the liters of sand settling in the same spigot from their sum. For the second spigot, add to the carrying current in spigot #1 the rising current in spigot #2 and deduct the liters of sand settling in spigot #2. Similarly for spigot #3. Line (13) equals Line 12 divided by Line 5. Line (14) equals Line 13 divided by 645. Line (15) equals \( \sqrt{\text{Line 14}} \). We will adopt 3-7/8", 10-1/2" and 13-3/4" to aid the carpenter work. Line (16) is assumed in the design. Line (17) is derived from relation \( V = \sqrt{2gh} \). Line (18) equals
Line 17 x 60. Line (19) gives the sizes of spigots assumed. Line (20) gives areas of same. Line (21) equals Line 20 multiplied by Line 18 and divided by 1,000,000. Line (22) is obtained by subtracting Line (6) from Line (21). Line (23) equals Line 22 multiplied by 0.26419. In the case of the overflow Line 7 is multiplied by 0.26419.

The classifier will make a spigot product assaying 47.7% B.P.L. and on the basis of 30% recovery in the washer will increase the total tonnage 170%.

The above B. P. L. content is too low to make the product salable but if raised to 50% by adding a small quantity of high grade rock will find a ready market for export to Japan.

The above computations have been tabulated on page 20.
#20.

**TABULATED COMPUTATIONS FOR HYDRAULIC CLASSIFIER.**

<table>
<thead>
<tr>
<th>FEED</th>
<th>1 Spigot</th>
<th>2 Spigot</th>
<th>3 Spigot</th>
<th>Overflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tons sand 24 hr.</td>
<td>100</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Sand sizes mm</td>
<td>3.00-0</td>
<td>3.00-1.06</td>
<td>1.06-0.70</td>
<td>0.70-0.42</td>
</tr>
<tr>
<td>Kgs. minute sand</td>
<td>63.1</td>
<td>15.8</td>
<td>15.8</td>
<td>15.8</td>
</tr>
<tr>
<td>Rising current mm/sec</td>
<td>----</td>
<td>95.6</td>
<td>72</td>
<td>43</td>
</tr>
<tr>
<td>&quot; &quot; &quot; /min</td>
<td>----</td>
<td>5.736</td>
<td>4.320</td>
<td>2.580</td>
</tr>
<tr>
<td>Liters sand/min</td>
<td>24.16</td>
<td>6.05</td>
<td>6.05</td>
<td>6.05</td>
</tr>
<tr>
<td>Water,liters/min</td>
<td>252.40</td>
<td>18.15</td>
<td>18.15</td>
<td>18.15</td>
</tr>
<tr>
<td>Total water,sand,liter</td>
<td>276.58</td>
<td>24.20</td>
<td>24.20</td>
<td>24.20</td>
</tr>
<tr>
<td>Area,section sorting column, sq. mms.</td>
<td>----</td>
<td>4.219</td>
<td>5.602</td>
<td>9.380</td>
</tr>
<tr>
<td>Size of pipe (theoretical)</td>
<td>----</td>
<td>2-7/8</td>
<td>3</td>
<td>5/16</td>
</tr>
<tr>
<td>Size of pipe (practical)</td>
<td>----</td>
<td>3</td>
<td>3 1/2</td>
<td>4</td>
</tr>
<tr>
<td>Carrying current sand and water liters/min</td>
<td>----</td>
<td>283.68</td>
<td>300.73</td>
<td>312.38</td>
</tr>
<tr>
<td>Pocket, sq.mm area</td>
<td>----</td>
<td>50.322</td>
<td>69.625</td>
<td>121.271</td>
</tr>
<tr>
<td>&quot; &quot; inch &quot;</td>
<td>----</td>
<td>78.03</td>
<td>106.0</td>
<td>188.0</td>
</tr>
<tr>
<td>&quot; side of sq.(inches)&quot;</td>
<td>----</td>
<td>8.83</td>
<td>10.40</td>
<td>13.70</td>
</tr>
<tr>
<td>The heights acting on spigots feet</td>
<td>----</td>
<td>2.2</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Vel.mm/sec due to height</td>
<td>5,527</td>
<td>3,779</td>
<td>3,932</td>
<td>----</td>
</tr>
<tr>
<td>Vel. mm/min &quot; &quot; &quot;</td>
<td>217,620</td>
<td>226,740</td>
<td>235,920</td>
<td>----</td>
</tr>
<tr>
<td>Spigots,diam, inches</td>
<td>1/2</td>
<td>1/2</td>
<td>3/8</td>
<td>----</td>
</tr>
<tr>
<td>Area sq. mm of spigots</td>
<td>127</td>
<td>127</td>
<td>71</td>
<td>----</td>
</tr>
<tr>
<td>Liters water &amp; sand min.</td>
<td>27.64</td>
<td>23.80</td>
<td>16.75</td>
<td>----</td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>21.59</td>
<td>22.75</td>
<td>10.70</td>
<td>----</td>
</tr>
<tr>
<td>Gals. &quot; &quot;</td>
<td>5.704</td>
<td>6.010</td>
<td>2.827</td>
<td>81.067</td>
</tr>
</tbody>
</table>
INVESTIGATIONS OF THE WRITER IN

MECHANICAL CONCENTRATION.

In order to decide which method of mechanical separation, if any, would be most suitable to the sample, it became necessary to ascertain the specific gravities of the pebble and matrix.

This determination gave the following results:

- Average grain of pebble rock: 2.72
- Colored grains: 2.88
- White grains: 2.63
- Sand grains: 2.61

These results gave little hope for a successful separation as it will be noticed that the specific gravities of the pebble rock and sand are almost identical.

I, however, decided to attempt a separation under hindered settling conditions by digging a sample of the sizes, larger than a 40 mesh screen aperture.

I used the Jarvis laboratory jig, as described in Vol. 39, pg. 451, of the Trans. Am. Inst. M.E., with a bed of coarse quartz, size on 8 mesh. The screen size was 12 mesh. The jig was adjusted to give a throw of 1/44 and to make 302 R.P.M. Samples from the skimmings hutch and feed analyzed as follows:

<table>
<thead>
<tr>
<th>Feed</th>
<th>47.7</th>
<th>B. P. L.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skimmings</td>
<td>50.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>Hutch</td>
<td>38.5</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Observations of the action of the feed while jiggings and the results of the analysis convinced me that there was no true separation taking place between the pebble rock and sand. The apparent separation evidenced by the increased B. P. I. content of the skimmings was due to removal of the fine sizes of both pebble and sand, through the bed and screen into the hatch caused by the suction stroke of the piston.

Successive adjustments of the bed, stroke and speed gave confirmation to this belief as without suction there was no stratification whatever.

As the feed was too fine to put on a Wilfley table, I experimented with a small quantity of rock and matrix in a glass beaker, simulating the action of a baffle or building table with negative results. Mr. Louis in his description of the plant previously referred to, does not give the specific gravities of the minerals to be separated so that it is impossible to judge whether the methods described would be applicable to our problem. The process he describes includes treatment on jigs and bullies which I find to be impracticable.

They, however, use hydraulic classification which I have found would be very desirable to apply to pebble rock as a sizing device only.

INVESTIGATIONS OF THE WRITER IN CHEMICAL TREATMENT.

I experimented in this direction by fusing common salt with the pebble, both ground to a fineness of 100 mesh, in a muffle furnace. My object was to produce a sodium acid phosphate, which is water soluble, according to the following reaction:

\[
\text{Ca}_3\text{P}_2\text{O}_8 + 5\text{SiO}_2 + 4\text{NaCl} + \text{H}_2\text{O} = 2\text{CaCl}_2 + 2\text{Na}_2\text{HPO}_4 + \text{CaSiO}_3
\]
1 gr. of salt to 2.76 grs. of rock, would theoretically be required but 40 grs. of salt to 100 grs. of rock was used to have excess of Chlorine. The salt and rock were thoroughly mixed, placed in an evaporating dish and subjected to a temperature of about 900°F in a muffle furnace for three hours. The mixture was then placed in a large beaker, water added and brought to a boil. The water was then decanted off and analyzed for \( P_2O_5 \). A number of such experiments were made but in every case the amount of \( P_2O_5 \) made soluble was inappreciable.

I believe that the temperature I was able to attain in the muffle furnace was too low to start the reaction and that the introduction of steam is very essential. The heat balance which follows shows that the reaction is an exothermic one, a surplus of 194,150 heat units being evolved.

<table>
<thead>
<tr>
<th>Heat required to decompose</th>
<th>Heat liberated by formation of</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Ca_3P_2O_8 ) ( = ) 919,200</td>
<td>( CaCl_2 ) ( = ) 339,800</td>
</tr>
<tr>
<td>( 4NaCl ) ( = ) 391,600</td>
<td>( 2Na_2HPO_4 ) ( = ) 904,800</td>
</tr>
<tr>
<td>( H_2O ) ( = ) 69,000</td>
<td>( CaSiO_3 ) ( = ) 329,350</td>
</tr>
<tr>
<td>( SiO_2 ) ( = ) 0</td>
<td>( ) ( 1,279,800 ) Heat units</td>
</tr>
<tr>
<td>( ) ( = ) ( 1,573,950 ) Heat units evolved</td>
<td></td>
</tr>
</tbody>
</table>

The high temperature needed to start the reaction can probably only be reached in an electric furnace. The products \( CaCl_2 \) and \( Na_2HPO_4 \) are both water soluble. \( CaSiO_3 \) is insoluble. The \( CaCl_2 \) would have to be precipitated out before evaporating the leaching solution to dryness.
CONCLUSIONS.

The writer believes from the results of his experiments that: sizing in a hydraulic classifier is the only practical method of treating the hitherto wasted product of the washers and that this system could be installed and operated economically in connection with the present methods of dressing to the very great advantage of the operators, as it not only utilizes a product which costs just as much to mine as the rock itself, and which can be sold as a low grade ore abroad or raised to a merchantable domestic grade either by the addition of a small amount of high grade rock or by the chemical treatment suggested by Dr. Wyatt.

The writer further believes that with the sulfuric acid at $6.00 a ton delivered in Florida and acid phosphate at $6.00 per unit or a guaranteed 16% available \( P_2O_5 \) basis, that all other chemical treatments if practical are too expensive to make them worthy of serious consideration.
A RESUME OF PATENTS, RELATING TO METHODS FOR TREATING
PHOSPHATE ROCK TO RENDER IT SOLUBLE (to Jan. 1911)

There have been a number of processes patented, a list of which is appended, with a view to the manufacture of soluble phosphates from the tricalcic phosphate by simple fusion with alkalis, as the alkali phosphates and acid phosphates are all water or citrate soluble. None of the processes have been commercially successful.

#74,799, Feb. 25, 1868, J. Commins,
"Improved mode of treating Mineral Phosphates for the manufacture of Fertilizer."

Mineral phosphates are heated to acid or white heat and saturated with a solution of common salt while hot to convert the phosphate into soluble form.

#78,061, May 19th, 1868, J. Commins,
"Improved Mode of Treating Mineral Phosphate for the Manufacture of Fertilizers."

Mineral phosphates are heated and plunged into gas liquor, combined with sulphuric acid or other acid or salt.

#128,752, July 9, 1872, N. Pratt, Charleston, S.C.
"Treating Phosphatic Rock."

Phosphatic material while being ground is treated with diluted acid and the obtained paste is squeezed out either by means of hydraulic presses or centrifugal machines.

"137,635, April 8, 1873, H. Storack, Asnieres, France,
"Manufacture of Acid Phosphates".
Soluble acid phosphates are produced by mixing phosphate of calcium with diluted phosphoric acid, precipitating the earthy matter by means of alkaline sulphates and extracting the sulphuric acid in the residual liquor by treatment with the phosphate of barium, lead or the carbonates of these bases.

#241,686, May 24, 1881, G. A. Fribeg, Balt.

"Treating Phosphates for Fertilizer."

Two parts of ground, crude phosphate rock are mixed with one part of coal, charcoal or other carbon and the mixture subjected to great heat which results in a mass containing a large percentage of phosphoric acid.


"Process of Making Phosphates."

Crude ground phosphates are mixed with the alkaline sulphates or carbonates and coal; the mixture is roasted at a temperature below the point of fusion whereby the insoluble phosphoric acid in the phosphate is converted into soluble form.

#332,604, May 8, 1883, S. Goodale, Saco, Me.

"Fertilizer."

Mineral phosphates are mixed with a carbonaceous substance moistened with sulphuric acid and subjected to a temperature not to exceed 621° F.

#525,076, Mar. 5, 1895, A. Pieper, Hamburg, Germany,

"Process of making Citrate Soluble Phosphates."

The characteristic feature of this process consists in treating the mineral phosphate simultaneously with an alkali lye and lime in such proportions that there will be two
equivalents of calcium oxide for each equivalent of phosphoric acid of the phosphate under treatment.

#542,080, July 2nd, 1895, D. Day, Washington, D.C.
"Process of Making Phosphates Soluble in Dilute Citric Acid."

A mixture of phosphate and calcareous base is heated above 1350° F, the point at which carbonic oxide is driven off. The operation is much facilitated by having a suitable percentage of silica present.

#588,266, Aug. 17, 1897, G. de Chalmot, Leakesville, N.C.
"Treatment of Phosphates."

The Inventor made the discovery that if natural phosphates are smelted in an electric furnace without the addition of a reducing agent, the phosphoric acid in them becomes soluble, (See 1901, #639/236.)

#589,197, Aug. 31, 1897, H. Stead, Middlesborough, Eng.
"Phosphate and Method of Making Same."

The process of increasing the solubility of normally insoluble phosphates consists in smelting them with silicious and calcareous matter in proportion to yield compounds containing the ratio of 310 tricalcic phosphate to between 38 and 116 of monosilicate of lime.

#601,039, Mar. 22, 1898, J. Wiborgh, Stockholm,
"Phosphate and Method of Making Same."

Method of manufacturing, from apatite, a fertilizer, which consists in heating to a red or yellow heat the apatite together with a matter containing sodium (or potassium) in proportion to yield a compound containing the ratio of about 426
of phosphoric acid to 560 of calcium oxide and from about 124 to 188 of sodium or potassium oxide.

§689, 236, Dec. 17, 1901, C. de Chalmet, Leakesville, N.C. Relates to the treatment of natural phosphates by mixing the same with silica and heating the mixture in an electric furnace removing the material from the furnace, as fast as it becomes molten and then bringing the heated material into contact with a further quantity of silica. The phosphoric acid which is driven off is conducted in contact with moist lime or phosphate rock or otherwise recovered. The phosphoric acid remaining in the molten residuum is in soluble form.

Consists in mixing the phosphate with water and acid sulphate of soda passing through the mixture a current of electricity and evaporating the water from the mixture.


Heating a mixture of natural phosphates, silicates of the alkalies and silicates of the alkaline earths to a temperature of not less than 1200° C at which temperature the materials are converted into a homogeneous mass of a fluid molten
state which when cold is citrate soluble.

"748, 523, Dec. 29, 1903, W. Palmer, Stockholm.

"Process of Manufacturing Manure from Apatite."

The process of making bicalcic phosphate consists in first electrolyzing a solution of a suitable salt (a mixture of chlorate and perchlorate of sodium) which disengages at the anode an acid forming with lime a soluble salt and at the cathode a basic hydrate, then subjecting mineral phosphate in a separate vessel to the action of said solution formed at the cathode to the acid solution of the phosphate to precipitate bicalcic phosphate.

"739, 438, May 9, 1905, F.J. Machalske, Brooklyn N.Y.,

"Process of Treating Phosphate Rock."

Heating to a high temperature a mixture of phosphate rock, salt and carbon to obtain phosphorus chlorides and a mixture of carbides of calcium and sodium.


Rock is treated with sulphurous acid which is recovered and used in treating new charges.

"922, 494, May 25, 1905, J. Lowman, Nashville, Tenn.

"Process of Making Fertilizing Material."

A mixture of pulverized phosphate rock, 1000 lbs., common salt, 250 lbs., dolomite 200 lbs., fluor spar 50 lbs., the mixture is well burned, mixed with water and again heated to about 800° F. for about 12 hours.
"Process of Making Fertilizer."

Consists in reducing 5 parts of phosphate rock to a fine powder, adding 1 part of caustic soda and 2 parts of quicklime and mix in water until the mixture assumes the consistency of thick mud and finally subjecting this mixture to a high degree of heat until the phosphoric acid becomes available.

"Manufacture of Fertilizer."

Refers to the manufacture of fertilizer from phosphate rock by converting same into an impalpable powder by burning and slackling the lime contained in the phosphate rock.

"Process of Making Fertilizer."

The process of conversion of insoluble phosphate of lime into citrate soluble form, by calcination with lime and alkali.
3 POCKET HYDRAULIC CLASSIFIER
FOR LAND PEBBLE PHOSPHATE ROCK TAILINGS.

Capacity: 100 tons per 24 hrs.
Products: Spigot "1: 3.00 - 1.06 mm.
          *2: 1.06 - 0.70 *
          *3: 0.70 - 0.42 *

R. deC. Greene 5/22/13
Longitudinal Section

Plan

POCKET HYDRAULIC CLASSIFIER
AND PEBBLE PHOSPHATE ROCK TAILINGS.

Capacity: 100 Tons per 24 hrs

Pits: Spigot 1: 3.00 - 1.086 mm.
      2: 1.06 - 0.70
      3: 0.70 - 0.42

R. deC. Greene, 9/22/13