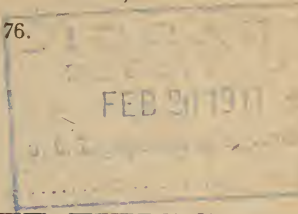


Historic, archived document

Do not assume content reflects current scientific knowledge, policies, or practices.

Issued February 16, 1911.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS—BULLETIN NO. 76.
MILTON WHITNEY, Chief.

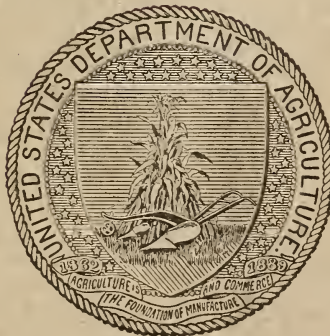


A REVIEW OF THE PHOSPHATE FIELDS OF FLORIDA.

BY

WILLIAM H. WAGGAMAN.

Scientist in Physical and Chemical Investigations.



WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1911.

BUREAU OF SOILS.

MILTON WHITNEY, *Chief of Bureau.*

ALBERT G. RICE, *Chief Clerk.*

SCIENTIFIC STAFF.

Frank K. Cameron, in charge of Physical and Chemical Investigations.

C. F. Marbut, in charge of Soil Survey.

Oswald Schreiner, in charge of Fertility Investigations.

W J McGee, in charge of Soil Water Investigations.

SCIENTISTS IN PHYSICAL AND CHEMICAL INVESTIGATIONS.

H. Bryan.

R. O. E. Davis.

G. H. Failyer.

C. C. Fletcher.

E. E. Free.

R. F. Gardner.

W. J. McCaughey.

W. B. Page.

H. E. Patten.

W. O. Robinson.

J. G. Smith.

C. C. Stark.

W. H. Waggaman.

Issued February 16, 1911.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS—BULLETIN NO. 76.
MILTON WHITNEY, Chief.

A REVIEW OF THE PHOSPHATE FIELDS OF FLORIDA.

BY

WILLIAM H. WAGGAMAN.
Scientist in Physical and Chemical Investigations.



WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1911.

LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS,
Washington, D. C., November 29, 1910.

SIR: I have the honor to transmit herewith the manuscript of a report covering the phosphate rock industry of Florida, and to recommend that it be published as Bulletin No. 76 of this Bureau. The report forms one of a proposed series of bulletins embodying the results of researches now being conducted by the Bureau on the phosphates of lime. These substances form the basis of fertilizer manufacture the world over, and are of the utmost importance in the intensive handling of the soil.

The work covered by the present article was done by Mr. William H. Waggaman, a chemist in the Bureau, who was associated during a part of the field season of 1910 with Mr. G. C. Matson, of the U. S. Geological Survey, in an investigation, for the U. S. Land Office, of the mineral resources of certain public lands in Florida. It is desired to acknowledge here the courtesy and assistance rendered by Mr. Matson and the officials of the organization named.

Respectfully,

MILTON WHITNEY,
Chief of Bureau.

HON. JAMES WILSON,
Secretary of Agriculture.

PREFACE.

Public attention has repeatedly been directed in the last few years to the phosphate deposits of this country. Grave fears have been expressed that a serious dearth of available phosphates is imminent, and that at a time when their importance, if not necessity, for the agricultural development of the country is coming to be appreciated. These fears are undoubtedly exaggerated, but the agitation has not been without some value. Phosphate deposits of greater or less extent and of varying degrees of richness are being reported from almost all parts of the country, and the most extensive deposit of high-grade rock in the world, lying in the States of Utah, Wyoming, and Idaho, is as yet practically untouched. Deposits have been reported in the States of Pennsylvania, New Jersey, New York, North Carolina, Arkansas, Kentucky, Nevada, and California, in addition to the well-known deposits of Tennessee, South Carolina, and Florida. Coincident with the discovery of new deposits in this country there has been considerable activity in the discovery and especially in the development of foreign deposits, notably those of northern Africa, the South Pacific Islands, France, and Belgium.

It is a debatable question whether there is any reason for fearing a world shortage of rock phosphate. But the situation is not without its serious economic aspects for this country. The Florida deposits are worked to an extent far outstripping all other American deposits and only approached by those of northern Africa. A large percentage of the best Florida rock is exported to Europe. Indeed, Europe takes only the high-grade rock, and this, together with the fact that Europe takes a larger proportion of high-grade Florida rock than does the United States, has led to alarming reports regarding the control of these deposits by foreign corporations. Foreign corporations are large operators in Florida, but they do not control a major part of the output, and no individual foreign-controlled plant is as large as some of those operated by American capital. A far more serious feature of the present situation is the waste of lower-grade rock, and even some high-grade rock, incident to the methods of mining. If for economic reasons the best rock must continue to go to foreign markets, it will soon be imperative to devise means of conserving and handling what is now wastage for the use of the home consumer.

That the present or any prospective exportation of rock phosphate is likely to impair seriously the resources of this country is very doubtful. The foreign market demands and can handle only the most expensive grades, and other deposits, such as those of the Ocean Islands, Tunis, and Algiers, are now supplying more to Europe than are the deposits of Florida. While it may be true that the end of the hard-rock deposits of Florida is in sight, this is certainly not the case with the pebble deposits, and the vast bulk of other American deposits has been scarcely touched. With the great mass of material in sight of medium or low grade, or unavailable to Europe on account of prohibitive land transportation rates, the great problem is to devise means and methods for making the material as readily available and as cheap as possible to the home consumer. This problem involves the elimination of waste or its reduction to the lowest possible point. At present it appears that this problem must be worked out in connection with the Florida deposits, and the résumé of the conditions now existing, which is given in the following bulletin, is not only valuable in itself, but is far more important as a basis for future investigations in the interests of American agriculture.

FRANK K. CAMERON,
In Charge Physical and Chemical Investigations.

CONTENTS.

	Page.
Introduction.....	7
Hard-rock phosphate	7
Location of deposits.....	7
Geological occurrence.....	9
Physical properties.....	9
Methods of mining.....	10
Washing the rock.....	11
Drying the rock.....	12
Cost of production.....	13
Freight rates.....	13
Disposal of product.....	14
Waste material.....	15
Utilization of waste material.....	16
Extent of operations.....	16
Present condition of the industry.....	17
Future of the industry.....	18
Pebble phosphate.....	18
Location of deposits.....	18
Geological occurrence.....	19
Physical properties.....	19
Methods of mining.....	20
Washing the rock.....	20
Drying the rock.....	21
Cost of production.....	21
Freight rates.....	22
Disposal of product.....	22
Waste material.....	22
Extent of operations.....	23
Present condition of the industry.....	23
Future of the industry.....	23
Summary.....	23

A REVIEW OF THE PHOSPHATE FIELDS OF FLORIDA.

INTRODUCTION.

By far the most extensively mined deposits of phosphate in this country are those of Florida. From 1888, when the first 3,000 tons of phosphate was shipped from the Peace River district, to 1909 the production of Florida phosphate rock steadily increased. Then, owing to various causes discussed further on in this bulletin, mining operations in the hard-rock phosphate regions fell off considerably. The production of land-pebble phosphate, however, has continued to grow uninterruptedly, until now the annual output is over 1,250,000 tons.

The two most important classes of phosphate in Florida at present are the hard-rock and the land-pebble phosphates. The river pebble, which was the first exploited, in the Peace River district, is no longer mined, owing to its low content of phosphate of lime. The soft phosphate which occurs intermixed with both the hard rock and the pebble phosphates is washed away in preparing the rock for the market.

HARD-ROCK PHOSPHATE.

LOCATION OF DEPOSITS.

The hard-rock phosphate regions lie toward the west side of the Florida peninsula, extending from Suwanee and Columbia Counties southward to Citrus and Hernando Counties—a distance of over 100 miles. Many of the mines are reached by both the Atlantic Coast Line and the Seaboard Air Line Railroads, or by spurs from these roads. The rock is hauled to the seaports on both the east and west coasts for shipment.

GEOLOGICAL OCCURRENCE.

The hard-rock phosphate belongs to the middle Tertiary or Oligocene epoch, and to the geological formation known as the Hawthorne. It occurs in irregular pockets which vary in size from a few square yards to several acres in extent. The rock is embedded in a matrix of sand, clay, and soft phosphate, the whole usually resting on a limestone of lower Oligocene age. In many of the dry mines, where

the phosphatic matrix has been removed, the pockety nature of the phosphate deposits is quite apparent. The pits contain numerous cones and columns of unaltered limestone, which present a very striking appearance.

The following summary, taken from the Second Annual Report of the Florida State Geologist for 1909, shows the overlying and underlying formations more or less directly related to the study of the phosphate beds:

Age.	Formation.																						
Pliocene (?)	Lafayette formation.																						
	Unconformity.																						
Pliocene	<table border="0" style="display: inline-table; vertical-align: middle;"> <tr> <td rowspan="4" style="font-size: 3em; vertical-align: middle;">}</td> <td>Bone Valley gravel (contains land-pebble phosphate)</td> <td rowspan="4" style="font-size: 3em; vertical-align: middle;">}</td> <td rowspan="4" style="vertical-align: middle;">Largely contemporaneous.</td> </tr> <tr> <td>Alachua clay</td> </tr> <tr> <td>Nashua marl (northeastern Florida)</td> </tr> <tr> <td>Coloosahatchee marl (south-central Florida)</td> </tr> </table>	}	Bone Valley gravel (contains land-pebble phosphate)	}	Largely contemporaneous.	Alachua clay	Nashua marl (northeastern Florida)	Coloosahatchee marl (south-central Florida)															
}	Bone Valley gravel (contains land-pebble phosphate)		}			Largely contemporaneous.																	
	Alachua clay																						
	Nashua marl (northeastern Florida)																						
	Coloosahatchee marl (south-central Florida)																						
	Unconformity (?)																						
Miocene	<table border="0" style="display: inline-table; vertical-align: middle;"> <tr> <td rowspan="2" style="font-size: 3em; vertical-align: middle;">}</td> <td>Jacksonville formation (east coast)</td> <td rowspan="2" style="font-size: 3em; vertical-align: middle;">}</td> <td rowspan="2" style="vertical-align: middle;">Contemporaneous.</td> </tr> <tr> <td>Choctawhatchee marl (western Florida, St. Johns Valley)</td> </tr> </table>	}	Jacksonville formation (east coast)	}	Contemporaneous.	Choctawhatchee marl (western Florida, St. Johns Valley)																	
}	Jacksonville formation (east coast)		}			Contemporaneous.																	
	Choctawhatchee marl (western Florida, St. Johns Valley)																						
	Unconformity.																						
Oligocene	<table border="0" style="display: inline-table; vertical-align: middle;"> <tr> <td rowspan="5" style="font-size: 3em; vertical-align: middle;">}</td> <td rowspan="4" style="vertical-align: middle;">Apalachicola group.</td> <td>Alum Bluff formation</td> <td rowspan="4" style="font-size: 3em; vertical-align: middle;">}</td> <td rowspan="4" style="vertical-align: middle;">Probably contemporaneous.</td> </tr> <tr> <td>Chattahoochee formation (western Florida)</td> </tr> <tr> <td>Hawthorne formation (contains hard-rock phosphate)</td> </tr> <tr> <td>Tampa formation (southern Florida)</td> </tr> <tr> <td>Unconformity.</td> <td></td> </tr> <tr> <td rowspan="3" style="font-size: 3em; vertical-align: middle;">}</td> <td rowspan="3" style="vertical-align: middle;">Vicksburg group.</td> <td>Ocala limestone</td> <td></td> <td></td> </tr> <tr> <td>Peninsula limestone (central Florida).</td> <td></td> <td></td> </tr> <tr> <td>Marianna limestone (western Florida).</td> <td></td> <td></td> </tr> </table>	}	Apalachicola group.	Alum Bluff formation	}	Probably contemporaneous.	Chattahoochee formation (western Florida)	Hawthorne formation (contains hard-rock phosphate)	Tampa formation (southern Florida)	Unconformity.		}	Vicksburg group.	Ocala limestone			Peninsula limestone (central Florida).			Marianna limestone (western Florida).			
}	Apalachicola group.			Alum Bluff formation			}	Probably contemporaneous.															
				Chattahoochee formation (western Florida)																			
				Hawthorne formation (contains hard-rock phosphate)																			
			Tampa formation (southern Florida)																				
	Unconformity.																						
}	Vicksburg group.	Ocala limestone																					
		Peninsula limestone (central Florida).																					
		Marianna limestone (western Florida).																					

Dall^a concludes that the phosphoric acid of the Florida rock is entirely derived from organic sources, probably from the dung of birds, seals, or other gregarious animals. Since Florida has probably always been a rainy region, the phosphoric acid was leached out of this organic material as fast as it was formed and taken up or fixed by the underlying limestone. He thinks it doubtful whether the frequent occurrence of bones and teeth has any bearing on the origin of the phosphate beds, since these animal remains occur in many other localities where the phosphate deposits are lacking.

Pratt^b differs from Dall as to the origin of the Florida hard rock. He thinks that the boulders and their fragments are the fossil remains of gigantic foramanifera which either perished through natural causes or were preyed upon by higher forms of marine life. In any event, their phosphatic substance went to form the present phosphate beds. He also suggests that the soft phosphate found in the matrix may be derived from the spawn of these prolific animals.

^a Bul. No. 84, U. S. Geological Survey, pp. 134-140 (1891).

^b An official report made on 8,000 acres of phosphate property in Florida (1890).

Eldridge ^a divides the formation of the hard-rock deposits into three periods: First, that in which the primary rock was formed from underlying limestones by displacement of carbonic acid by phosphoric acid; second, that of secondary deposition in the cavities of the primary rocks; and third, that in which the deposits thus formed were broken up and mixed with foreign material by the last submerging of the peninsula.

Jumeau ^b attributes the formation of the Florida phosphates to the secretion and subsequent deposition of phosphate of lime by lower marine forms which found favorable conditions for growth in the sheltered bays and estuaries of this peninsula; to the excreta of birds which fed on marine life; and to the deposition of innumerable bones resulting from the death of higher forms of animals driven south by the intense cold of the glacial period.

PHYSICAL PROPERTIES.

The hard-rock phosphate varies widely in its physical properties. In color the rock ranges from almost jet black to a dazzling white, and between these two extremes there are many shades.

Some specimens of rock are close grained, massive, and platelike, ringing when struck, while other samples are porous, light, and distinctly nodular. Most of the rock, however, is white or cream colored and is usually close grained, massive, and nodular in form, the last-named characteristic being due probably to attrition. Analyses showing the phosphoric-acid content of various types of rock are given in Table I.

TABLE I.—Composition of the different varieties of phosphate from the hard-rock region.

Sample No.	Location.	Description.	Analysis.				
			SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	P ₂ O ₅ .	Ca ₃ (PO ₄) ₂ .
4-B	Dunnellon..	Blue, hard (nodular).....	2.28	0.64	0.70	37.46	82.2
5-Bdo.....	White, hard (nodular).....	1.32	.32	.80	38.48	84.4
100	Anthony.....	White, hard (plate rock).....80	.73	34.5	75.6
101	Newberry....	Brown, hard (irregular).....	.72	12.80	4.38	34.3	75.5
102do.....	Red, soft (earthlike).....	.87	11.68	4.68	30.8	67.5

METHODS OF MINING.

Florida rock phosphate is mined by first removing the over burden of sand and clay and then digging out or dredging the phosphate thus exposed. The amount of overburden varies considerably, and the expense of mining largely depends on its character and thickness. The overburden is removed by scrapers, steam shovels, or hydraulic pumps, the last method being the one usually employed.

^a Trans. Amer. Inst. Mining Eng., vol. 21, pp. 196-251 (1891).

^b Le Phosphate de Chaux et Les Exploitations Aux Etats-Unis en 1905. Veuve Ch. Dunod, editeur, Paris.

In the dry mines, the phosphate-bearing material is ordinarily removed with pick and shovel, blasting being sometimes employed to break up the large boulders. There is less waste material sent to the washer from the pits of a dry mine, since the rock is to a certain extent sorted before loading into the cars. A dry mine does not require the same outlay of capital as a dredge mine, but does require more labor and often has to be closed down during wet weather. In a dredge mine, on the other hand, the phosphate deposits lie below the water level, so that considerable material containing a very low percentage of phosphate rock is scooped out and washed. Any breaking of the dredge necessitates the closing down of the washer until the damage is repaired. In a dredge mine, however, work is not stopped by wet weather.

In the vicinity of Anthony, Marion County, the hydraulic method of mining has been employed, but this is not usually practiced in the hard-rock regions, since the fragments of phosphate are often too large to be handled by an 8-inch centrifugal pump.

WASHING THE ROCK.

The phosphatic material is brought from the mines in tram cars and dumped on an iron grating, having bars 2 to 2½ inches apart, which allows the smaller pieces, together with the foreign material, to pass through into the washer. The larger lumps are put through a crusher and thence also pass into the washer. The washer usually consists of a pair of wooden cylinders, ordinarily logs, 30 feet in length and 18 inches in diameter, laid side by side in a kind of trough, one end of which is elevated about 2 feet above the other. A series of blades or teeth are fastened to the cylinders in the form of a spiral. The rock and earthy matrix enter the washer at the lower end, which is submerged in water. As the logs revolve, the material is pushed forward by the steel blades with constant rubbing, meeting streams of water flowing from the upper end of the washer, which cause the separation of the sand, clay, and soft phosphate from the hard rock. This fine material flows back to the lower end of the washer and is discharged upon a waste pile at some distance from the plant. Often the first two cylinders are followed by two more, and sometimes by a single cylinder only. A cleaner and higher-grade product is thus obtained, but the waste material is proportionately richer in phosphoric acid.

From the washer the rock passes into a revolving rinser for further cleansing. The rinser usually consists of a double-shell cylinder, 12 to 14 feet long. The inner shell is made of steel plate, with perforations three-eighths inch by 1½ inches, and the outer shell with perforations one-sixteenth inch by one-eighth inch. The cylinder is set on an incline. The rock from the log washers enters the inner

shell at the higher end of the rinser and is slowly rolled toward the exit end, jets of water spraying it continuously. Any loose sand and clay still clinging to the rock is washed away during this process. The finer rock falls through into the outer shell of the cylinder and is discharged into conveyors or carried to the wet bins in tram cars. The coarser rock is discharged from the inner shell of the cylinder upon a revolving platform, termed the picking table, where a number of boys and men pick out the clay balls, flint, and limestone. The phosphate rock is then swept from the table by scrapers and also carried to the wet bins or drying sheds.

DRYING THE ROCK.

The phosphate rock is dried either by kiln burning or in mechanical (rotary) driers. In the hard-rock regions the kiln method of drying is still largely employed. The kilns consist of long wooden sheds, open at the sides. The floor is first covered with a layer of phosphate rock about 2 feet thick, upon which pine logs are laid to a depth of $2\frac{1}{2}$ to 3 feet. The wet phosphate rock is then piled upon the logs to a height of 10 to 14 feet, and the wood is fired. Since the flames are partly smothered by the rock, the burning process is very slow and the heat spreads throughout the whole mass. At the end of a week the rock is pretty thoroughly dried and ready for shipment.

The mechanical method of drying is used by some of the larger phosphate operators in the hard-rock district, and is the only method used in the pebble regions. The rotary drier consists of a rotating steel cylinder, provided on the interior with longitudinal shelves, the whole being set on a gentle slope. The flame and gases from the furnace enter at the upper end and are drawn through the cylinder by a powerful draft. The rock is automatically fed in at the same end, and as the cylinder revolves it is caught up by the shelving and showered repeatedly through the flame and gases of combustion. It is discharged at the lower end, more or less thoroughly dried.

Another type of mechanical drier installed at one of the phosphate plants consists of a double-shell cylinder, the flame being drawn through the inner shell and the rock fed into the outer one. It is claimed by some that there is less loss of heat through radiation in this form of drier. In drying the phosphate rock a certain amount of the carbonate of lime present is probably reduced to oxide. The percentage of phosphorus in the finished product, therefore, is not only increased because of the moisture expelled, but also because of the carbon dioxide evolved.

In Table II are given the results of chemical analyses of two kinds of hard-rock phosphate, both before and after calcining. The samples were not large, however, so too much importance should not be given the figures. Indications point to an apparent enrichment after burn-

ing. All the samples were dried in the laboratory at 100° C. for at least four hours.

TABLE II.—*Chemical analyses of samples of hard-rock phosphate before and after burning.*

Sample number.	Description.	Analysis.	
		P ₂ O ₅ .	Ca ₃ (PO ₄) ₂ .
4-A	Blue rock, hard (not burned)	37.5	82.12
4-B	Blue rock, hard (burned)	37.5	82.12
5-A	White rock, hard (not burned)	37.1	81.25
5-B	White rock, hard (burned)	38.5	84.32

In some sections of the hard-rock region, where considerable phosphate of alumina occurs, the rock is screened after burning. It is claimed that this screening reduces the percentage of iron and alumina and raises the grade of the rock. In order to see if this would hold true under ordinary conditions where the deposit contained no abnormal amount of aluminum phosphate, the author collected samples both of medium-sized and of small fragments (not larger than a pea) from the same pile of burned rock and analyzed them. The results are given in Table III.

TABLE III.—*Chemical analyses of samples of large and small pieces of hard-rock phosphate after burning.*

Sample.	Location.	Description.	Analysis.				
			SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	P ₂ O ₅ .	Ca ₃ (PO ₄) ₂ .
3-A	Dunnellon....	Nodular, hard, fairly large lumps.	1.70	0.33	1.16	37.1	81.25
3-Bdo.....	Small fragments.....	4.37	.33	1.36	35.8	78.40

It will be seen from inspection of this table that both the silica and the iron and alumina are higher in the sample of small fragments than in that composed of larger pieces. The difference in the quality of the two samples is not only due to the disintegration of the aluminum phosphate but also to the fact that the larger pieces are sorted and many impure pieces thus eliminated.

COST OF PRODUCTION.

It is rather difficult to strike an average of the cost of preparing hard-rock phosphate for the market, the expense of mining and washing the rock being dependent upon a number of factors, two of which vary between rather wide limits. These two factors are the amount and character of the overburden and the richness and character of the phosphate deposits. The overburden may vary in depth from a

few inches to 30 feet or more, and in texture from a loose sand, costing but a few cents per cubic yard to remove, to a heavy clay, which is both difficult and expensive to handle. A conservative estimate of the average cost of removing overburden throughout the hard-rock district is from 12 to 15 cents per cubic yard. The phosphate deposit, on the other hand, may contain from 3 or 4 per cent to 90 per cent of phosphate rock, and may be composed chiefly of heavy clay, difficult to wash out, or of a light sand, which is readily washed away.

A former phosphate operator of wide experience informed the author that he had mined rock phosphate as low as 90 cents a ton and as high as \$10 a ton. It is probably safe to say that the average cost of the finished product f. o. b. at the mines is not less than \$3.50 a ton.

FREIGHT RATES.

The freight rates from the principal mining districts in the hard-rock region to the various shipping points on the east and west coasts of the peninsula are approximately as follows:

TABLE IV.—*Freight rates on phosphate rock.*

Location of mines.	Shipping point.	Freight rates.	
		Raw rock.	Dried rock.
Newberry and vicinity.....	Jacksonville.....	\$0.90	\$1.25
	Fernandina.....	.90	1.25
	Port Tampa.....		1.65
Dunnellon and vicinity.....	Jacksonville.....	1.10	1.35
	Fernandina.....	1.10	1.35
	Port Tampa.....		1.25
	Port Inglis.....	.80	
Inverness } Floral City } Istachatta } Anthony }	Jacksonville.....		1.35
	Fernandina.....		1.35
	Port Tampa.....		.85
	Jacksonville.....		1.80
	Fernandina.....		1.25
	Port Tampa.....	(a)	(a)

a No rate published.

DISPOSAL OF PRODUCT.

The hard-rock phosphate produced in Florida is almost entirely shipped abroad. Most of it is sold on a guarantee of 77 per cent phosphate of lime, a maximum of 3 per cent iron and alumina, and less than 3 per cent of moisture. A lower-grade rock than the above is shipped to Italy and France, but the English and German markets demand the higher grade material. A considerable quantity of the screenings obtained after putting the rock through the rotary driers is utilized in this country for the manufacture of superphosphate.

WASTE MATERIAL.

In order to meet the present demand for a high-grade product, a vast amount of phosphatic material is thrown aside. The marketed product is probably not more than 15 per cent of the total material mined. The remainder, consisting of sand, clay, and the phosphates of lime, iron, and aluminum, is washed out upon a waste pile. This discarded material varies in its content of phosphoric acid, but seldom if ever contains less than 10 per cent. The actual amount of phosphoric acid discarded, therefore, is almost twice as great as the quantity saved. This enormous amount of low-grade phosphate will no doubt eventually be used. A cheap solvent to take out the phosphoric acid would probably prove the means of putting some of it on the market immediately. Even in its present state this finely divided material would be of value if applied to the land in place of the more expensive ground rock or bone. On muck soils containing but little mineral phosphates, such for example as exist in the Florida Everglades, heavy applications of this phosphatic waste should be of considerable benefit.

Samples taken from various parts of the waste pile differ greatly in composition, as considerable mechanical separation takes place when the stream of water carrying this detritus is discharged upon the waste heap, because the clay and soft phosphates being held in suspension longest are carried some distance, while the sand and heavier particles are deposited more rapidly.

In order to get a better idea of its actual composition the author carefully washed some of the phosphatic detritus as it was brought from a prospect hole. The wash water and all material finer than 1 mm. were saved, and after evaporating the water the sample was thoroughly dried and mixed. The analyses of this material, together with some made by other chemists, are given in Table V.

TABLE V.—*Chemical analyses of material washed away in preparing hard rock for the market.*

Sample number.	Location.	Analyst.	Analysis.				
			SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	P ₂ O ₅ .	Ca ₃ (PO ₄).
6	SW. $\frac{1}{4}$ sec. 30, T. 15, R. 23 E.	Author.....	38.40	19.17	2.25	18.00	39.42
	Anthony.....	P. Jumeau.....	58.95	11.70	12.70	28.21
	do.....	do.....	60.10	11.20	12.20	26.72
	Newberry, 5 miles southeast	In office of Florida State chemist.	9.99	21.78
	Dunnellon.		12.14	26.59

Another source of waste in preparing Florida hard rock for the market is at the picking tables, where the washed material is picked over and the clay balls, limestone, and siliceous fragments are

removed and thrown aside. Inexperienced and careless pickers often throw away a great deal of good rock. Indeed it is sometimes difficult for the most experienced men to tell the good material from the bad.

An analysis of a sample of the so-called refuse from a picking table is given in Table VI.

TABLE VI.—*Chemical analyses of a sample of material thrown from picking tables.*

Sample No.	Location.	Description.	Analysis.				
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	Ca ₃ (PO ₄) ₂
1	Dunnellon....	Clay balls, limestone, etc.....	68.02	3.80	0.48	11.6	25.40

UTILIZATION OF WASTE MATERIAL.

In utilizing low-grade rock and also in manufacturing concentrated phosphatic fertilizers, operators in European countries first extract the phosphoric acid with enough sulphuric acid to precipitate the lime as calcium sulphate and then use this acid solution to treat a second quantity of phosphate rock.

The author has conducted a few preliminary experiments along these lines with a view to utilizing the waste material from the Florida mines. Samples of phosphatic waste (No. 6, Table V) were treated with sulphuric acid of three different strengths, specific gravity 1.60, 1.56, 1.42. These mixtures were thoroughly stirred and allowed to settle for 18 to 20 hours. The clear solution above the suspended matter was then decanted and analyzed. It was found that considerably more of the solution could be decanted clear from the acid of specific gravity 1.56 (ordinary chamber acid) than from the other two acid solutions. This acid was also found to be quite efficient in dissolving out the P₂O₅ from the waste. Acid of this strength, therefore, was used in the following experiment:

To 150 c. c. of sulphuric acid (specific gravity 1.56) 20 grams of waste material were added and the whole thoroughly mixed and allowed to settle for 18 to 20 hours. About 60 per cent of the total solution added (90 c. c.) could then be decanted clear. Part of this was analyzed to find out how efficient was the extraction and the remainder was mixed with a fresh sample of waste material in the same proportion as above. This procedure was carried out three times. Numbers 1, 2, and 3, in Table VII, show the composition of the solution after each treatment.

TABLE VII.—*Chemical analyses of sulphuric-acid solution after repeated treatments of phosphatic waste.*

Per cent in solution.						Per cent extracted from waste by each solution.				
Solution.	SiO ₂ .	Al ₂ O ₃ and Fe ₂ O ₃ .	CaO.	P ₂ O ₅ .	SO ₄ .	Solution.	SiO ₂ .	Al ₂ O ₃ and Fe ₂ O ₃ .	CaO.	P ₂ O ₅ .
No. 1.....	0.06	0.70	0.05	2.06	81.92	No. 1....	0.46	5.25	0.34	15.12
No. 2.....	.08	1.28	.05	3.96	77.04	No. 2....	.57	4.38	.06	14.53
No. 3.....	.49	2.31	.04	5.74	74.84	No. 3....	3.12	7.66	13.35

Comparing the figures in Table VII with the analyses of waste material used (Table V, No. 6) it will be noticed that while the ordinary chamber acid is a very efficient solvent for the phosphoric acid (P₂O₅) contained in the waste, it also dissolves out considerable quantities of iron and alumina (Fe₂O₃ and Al₂O₃) which are regarded as very objectionable in the manufacture of acid phosphate. On the other hand, it will be seen that the largest quantity of iron and alumina extracted by any of the three treatments with sulphuric acid is less than 15 per cent of the total quantity present in the waste; while the minimum amount of phosphoric acid dissolved is nearly 75 per cent of the total quantity present.

Thorp ^a states that the objectionable iron and alumina can be precipitated as phosphates by concentrating the acid solution by evaporation. This procedure entails some expense, however, and also causes a loss of phosphoric acid. More work along these lines will probably prove of economic importance.

EXTENT OF OPERATIONS.

During the early part of 1910, when the author visited the hard-rock region, there were twenty companies engaged in or waiting to renew mining operations. Five of these companies were controlled by foreign capitalists. The combined annual capacity of the foreign producers, however, did not exceed 150,000 tons, while the capacity of plants owned by the American interests exceeded 600,000 tons per annum.

PRESENT CONDITION OF THE INDUSTRY.

Owing to the low price of hard-rock phosphate during the latter part of 1909 and the early part of 1910, mining operations were at a rather low ebb, many mines being shut down. Rock which sold as high as \$10 to \$10.25 f. o. b. at the ports in 1908 declined to \$7.50 and \$8. There are several causes assigned for the decided drop in the price of hard-rock phosphates, but probably the most important

^a Outlines of Industrial Chemistry, p. 153.

ones are the large shipments of phosphate from Ocean and Christmas Islands and the production of very high grade pebble phosphate in Polk and Hillsboro Counties.

The phosphate rock from the Pacific islands is richer than any yet discovered, averaging from 80 to 85 per cent tricalcium phosphate. It can be mined very cheaply, but until the last year high freight rates have kept the product out of the market. A number of land-pebble companies in southern Florida are now shipping material containing from 72 to 75 per cent tricalcium phosphate. The cost of mining pebble phosphate is about one-half as great as that of mining hard rock. A mixture of two parts of pebble with one part of the Ocean Island phosphate will give a product equal in richness to the hard-rock phosphate, and at a less cost.

The following figures, taken from the reports of Van Horn^a and Sellards,^b show the production of phosphate rock in the hard-rock regions during the last three years:

TABLE VIII.—*Production and shipments of Florida hard rock.*

Year.	Pro- duction.	For use in United States.	Exported.	Total shipments.
	<i>Tons.</i>	<i>Tons.</i>	<i>Tons.</i>	<i>Tons.</i>
1907.....	768,011	9,900	631,001	646,000
1908.....	527,582	17,456	496,645	640,900
1909.....				514,101

FUTURE OF THE INDUSTRY.

The operators in the hard-rock regions regard the present low price of phosphate as abnormal, and due to overproduction. They have, therefore, cut down their output considerably and are waiting for the market to assume its normal condition. It seems doubtful, however, that the price will advance for some time, for new fields have been recently discovered in other sections of this country which compare favorably in richness and far surpass in tonnage the hard-rock phosphate of Florida. The life of the hard-rock phosphate deposits has been estimated many times, but in each case new deposits have been discovered subsequently, which has upset all calculations. The phosphate operators, however, no longer regard the supply as inexhaustible, for very few new deposits are being discovered, and many of the old ones have been worked out. The end of the hard-rock industry in Florida is variously estimated from 25 to 100 years, depending on the rate of production.

^a Mineral Resources, U. S. Geological Survey, 1909.

^b Production of Phosphate Rock in Florida, Florida Geological Survey, 1909.

PEBBLE PHOSPHATE.

Development of the pebble deposits began in 1890. These were not at first considered as important as the hard-rock deposits, owing to their lower content of phosphoric acid. Their exploitation has steadily progressed, however, and within the last few years the output has increased so rapidly that now the annual shipments far surpass those from the hard-rock regions. In 1909 the shipment of pebble phosphate was 47 per cent greater than in the preceding year.

Improved methods of mining and treating the material have made it possible to place on the market a product which has a content of phosphoric acid but little below that of hard-rock phosphate. Since the pebble deposits are much more regular than the hard rock, and the actual mining can be carried on more cheaply, these deposits are eagerly exploited.

LOCATION OF DEPOSITS.

The land-pebble phosphate deposits, which are at present productive, lie south of the hard-rock regions, in Polk and Hillsborough Counties. The material is chiefly shipped to Port Tampa, 30 to 75 miles distant.

GEOLOGICAL OCCURRENCE.

The land-pebble phosphate belongs to the Pliocene epoch or late Tertiary and to the geologic formation known as the Bone Valley gravel. The deposits are much more regular than the hard-rock phosphates, lying in sheets of varying thickness. The pebbles are embedded in a sand and clay matrix similar to that found in the hard-rock regions. Darton^a says that the land pebble is undoubtedly derived from the rock phosphate, since the pebbles are similar in appearance to the hard rock and overlap these older beds as a shore deposit. Eldridge^b also thinks that the pebble deposits are probably composed of the rolled fragments of preexisting beds, but is doubtful if they are derived from the hard-rock phosphate. In discussing the origin of the land-pebble phosphate Eldridge quotes from an unpublished paper of Shaler, in which the author attributes the formation of phosphate pebbles to the leaching action of phosphate solutions upon soft, porous marls, the replacement of carbonic by phosphoric acid being accompanied by a certain degree of disintegration. The fragments thus formed when subjected to some concretionary deposition and attrition assumed a pebble form. This author further states that it is evident the pebble deposits have been subjected to erosive forces, since the beds in the valleys are much

^a Amer. Jour. Mining Eng., vol. 41, p. 105 (1891).

^b Amer. Jour. Mining Eng., vol. 21, pp. 218-219 (1892).

thicker than those in the uplands. The frequent occurrence of sharks' teeth and other marine remains indicate that this erosion was caused by the action of the sea.

PHYSICAL PROPERTIES.

The land-pebble phosphate, like the hard-rock, varies considerably in its physical properties. The pebbles range in size from those as large as a hickory nut to material too fine to be held by a screen of one-sixteenth-inch mesh. In color the pebbles vary from black to white, and between these two extremes there are many intermediate shades of yellow, brown, and gray. As a whole, however, the pebbles are light colored and considerably softer than the hard-rock phosphate. They are often quite porous and consequently lighter, bulk for bulk, than the hard rock.

In Table IX are given the analyses of three different colored samples. It will be noted that the black pebbles and white pebbles are richer in phosphoric acid than the brown or yellow. This same appears to be true in the hard-rock regions.

TABLE IX.—*Chemical analyses of samples of different colored pebble phosphate, from Mulberry, Fla.*

Sample No.	Location.	Description.	Analyses.				
			SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	P ₂ O ₅ .	Ca ₃ (PO ₄) ₂ .
202	Mulberry.....	Small black pebbles.....	4.66	0.34	0.96	35.40	77.53
203do.....	Small white pebbles.....	4.16	.60	.80	34.60	75.77
204do.....	Small brown pebbles.....	3.81	.84	2.24	31.30	68.55

METHODS OF MINING.

The hydraulic method of mining has practically displaced all other methods in the pebble regions. Streams of water 1½ to 2 inches in diameter, and under a pressure of 100 to 125 pounds per square inch, eat their way into the banks of phosphate, washing the material down to an 8-inch centrifugal pump, which forces it to the washer plant for subsequent treatment. Often two of these pumps are necessary to raise the material to the required height. The overburden is usually removed in the same way, though sometimes a steam shovel is employed.

WASHING THE ROCK.

Various schemes are employed for washing the pebbles free from foreign material, but the plan in general use is as follows: The 8-inch stream containing the gravel and other materials is discharged into a revolving screen having perforations 1½ by 2 inches in diameter. All lumps (clay balls) and fragments which will not pass through these perforations are discharged at the lower end of the screen and

carried away to a waste heap. The remainder of the material passes through a series of log washer sand rinsers, where it is submitted to the same cleansing process as used in case of the hard-rock phosphate. The logs, however, are shorter and not so heavy as those used in washing hard rock. The cleansed pebbles are finally discharged at the lower end of the washer and carried by tramcars or conveyers to the drying plant. In order to raise the final product to a grade of 74 or 75 per cent of tricalcium phosphate a picking table is sometimes employed; but this is not generally used, since most of the material is so fine that it is difficult to distinguish the clay balls and siliceous fragments from the phosphate. At one of the plants, to attain this same end, the material after a preliminary washing is put through a crusher which mashes the clay balls so that they are easily disintegrated by subsequent washings.

DRYING THE ROCK.

The rotary cylinder method described under hard-rock phosphate is used in drying the pebble phosphate.

In Table X analyses of the coarse and fine pebbles after the drying process are given. It will be seen that here again the coarse material is richer in phosphoric acid than the fine.

TABLE X.—*Chemical analyses of samples of coarse and fine phosphate pebbles.*

Sam- ple No.	Location.	Description.	Analyses.				
			SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	P ₂ O ₅ .	Ca ₃ (PO ₄) ₂ .
200	Mulberry.	Coarser than 2 mm. . . .	6.19	0.73	1.60	32.5	71.27
201do.....	Finer than 2 mm.	7.45	1.04	1.28	31.6	69.20

COST OF PRODUCTION.

The cost of preparing pebble phosphate for the market depends largely on the same factors which affect the cost of mining hard-rock phosphate. Owing to the greater uniformity of the pebble deposits, however, and to the fact that the material can be handled by centrifugal pumps, the pebble phosphate can be more readily and cheaply mined. The average cost of mining and preparing the pebbles for the market can also be more readily determined, since mining operations are conducted on a much more extensive scale than in the hard-rock regions. A conservative estimate of the cost of the finished product f. o. b. at the mines is about \$2 a ton.

FREIGHT RATES.

The freight rates from the principal mining districts to the various shipping points in Florida are given in Table XI.

TABLE XI.—*Freight rates on pebble phosphate.*

Location of mines.	Shipping point.	Freight rates per ton.
Pierce, Agricola, McDowell's.....	Tampa.....	\$0.50
	(Jacksonville).....	1.80
	Fort Tampa.....	.50
Mulberry and vicinity.....	(Jacksonville).....	^a 2.00
	Fernandina.....	2.09

^a Ton of 2,000 pounds.

DISPOSAL OF PRODUCT.

The land-pebble phosphate is used both in this country and abroad, the shipments for domestic consumption being about one-half of the total output. The product is sold on guarantees ranging all the way from 60 to 75 per cent of tricalcium phosphate. A maximum of 3 per cent of moisture and 3.5 to 4 per cent of combined iron and alumina are allowed. The 70 to 75 per cent material is practically all sold abroad. A small quantity of lower grade product (60 to 65 per cent) is shipped to Japan. The pebbles are largely used in this country for the manufacture of acid phosphate. Many of the companies operating in these regions have extensive fertilizer interests and utilize much of the output from their mines.

Table XII, table compiled from the report of Van Horn ^a and that of Sellards, ^b shows the production of pebble phosphate during the last three years.

TABLE XII.—*Production and shipments of pebble phosphate in tons during 1907, 1908, and 1909.*

Year.	Production.	Used in United States.	Exported.	Total shipments.
	<i>Tons.</i>	<i>Tons.</i>	<i>Tons.</i>	<i>Tons.</i>
1907.....	1,150,000	421,781	470,270	675,000
1908.....	1,334,000	819,761	509,341	900,000
1909.....				1,329,000

WASTE MATERIAL.

The percentage of phosphoric acid washed away in preparing pebble phosphate for the market is fully as great as that wasted in mining hard-rock phosphate. In the vicinity of the large phosphate washers many acres are covered to a considerable depth with this detritus. The author made no determination of the exact composition of this finely divided material, but it resembles the wash from the hard-rock mines, analyses of which are given in

^a Mineral Resources, U. S. Geological Survey, 1909.

^b Production of Phosphate Rock in Florida, State Geological Survey, 1909.

Table V. An analysis, however, was made of the material having a diameter greater than $2\frac{1}{2}$ inches discarded before the material containing the phosphate goes through the washing process. The composition of a sample thrown from the picking table at one of the plants was also determined. These analyses are given in Table XII.

TABLE XII.—*Chemical analyses of discarded material.*

Sam- ple No.	Description.	Analysis.				
		SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	P ₂ O ₅ .	Ca ₃ (PO ₄) ₂ .
205	Clay balls, $2\frac{1}{2}$ inches in diameter, containing phosphate pebbles from discard.....	<i>Per cent.</i> 44.10	<i>Per cent.</i> 5.24	<i>Per cent.</i> 1.78	<i>Per cent.</i> 17.6	<i>Per cent.</i> 38.54
206	Material from picking table.....	50.58	5.18	12.96	7.2	17.68

EXTENT OF OPERATIONS.

During the early part of 1910 there were 15 companies at work in the pebble-phosphate regions. Most of these were engaged in mining operations, the plants being run in two shifts of 10 to 12 hours each. Only two of the companies were controlled by foreign capitalists, and the combined capacity of these did not exceed 65,000 tons per annum. The total capacity of the present mines in the pebble regions is about 1,500,000 tons.

PRESENT CONDITION OF THE INDUSTRY.

The present condition of the pebble-phosphate industry is excellent. An inspection of Table XII will show the great increase in the production of land pebble during the past three years. Owing to the fact that it can be cheaply mined, the serious drop in the price of phosphate rock which occurred in 1909 did not cripple the pebble industry. On the contrary, there was a most substantial gain in the production over that of the previous year. The present price of the product f. o. b. at the mines is from \$2.75 to \$4.25 per ton, depending on the grade of rock.

FUTURE OF THE INDUSTRY.

With the growing demand for phosphatic fertilizers the increase in the production of land-pebble phosphate bids fair to continue. It is probable that the annual output will soon surpass 2,000,000 tons. These deposits are regarded as practically inexhaustible. This term is somewhat misleading and simply means that, in spite of the enormous production, the end of the pebble deposits is not as yet even in sight.

SUMMARY.

There are two commercially important classes of phosphate rock in Florida—the hard-rock phosphate and the land-pebble phosphate.

The hard-rock phosphate fields extend north and south along the west coast of the peninsula for a distance of 100 miles. The present land-pebble phosphate regions lie south of the hard-rock fields, in Polk and Hillsboro Counties.

Both the hard-rock and pebble deposits of phosphate belong to the Tertiary period. The methods of mining these two classes of phosphate rock differ considerably. In the hard-rock workings the material is either dug out or dredged. In the pebble deposits hydraulic mining is employed.

Practically all the hard-rock phosphate is shipped abroad and sold on a guarantee of 77 per cent tricalcium phosphate. The pebble phosphate is used both in this country and abroad, being sold on guarantees ranging from 60 to 75 per cent tricalcium phosphate.

In order to remove the impurities the material which comes from the mines is put through a washing process, during which much valuable phosphate is washed away. It is estimated that the actual amount of phosphoric acid lost in preparing the rock for the market is nearly twice as great as the quantity saved.

Possible means of utilizing this waste material are suggested, namely, to apply it to muck soils deficient in phosphoric minerals or to extract the phosphoric acid from it by means of a cheap solvent.

The average cost of preparing hard-rock phosphate for the market is not less than \$3.50 per ton, while the finished pebble product costs about \$2 per ton.

Early in 1910 there were 20 companies operating in the hard-rock regions, with a total annual capacity of more than 750,000 tons.

In the pebble regions 15 companies were engaged in mining operations, with a capacity of 1,500,000 tons per annum.

Owing to various causes the hard-rock industry was at a rather low ebb during 1909 and 1910, many plants being entirely closed down, but the operators expect the situation to improve.

The pebble industry, however, has been growing uninterruptedly and promises to continue to increase.

The life of the hard-rock phosphate is variously estimated to be from 20 to 100 years; the deposits of land-pebble phosphate are considered almost inexhaustible.

